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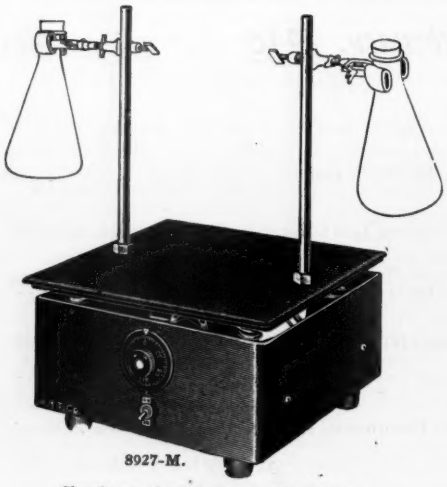

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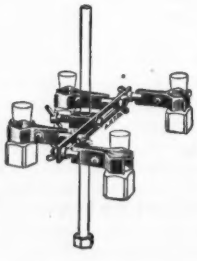

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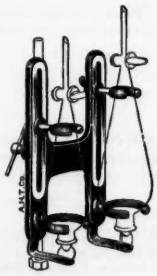

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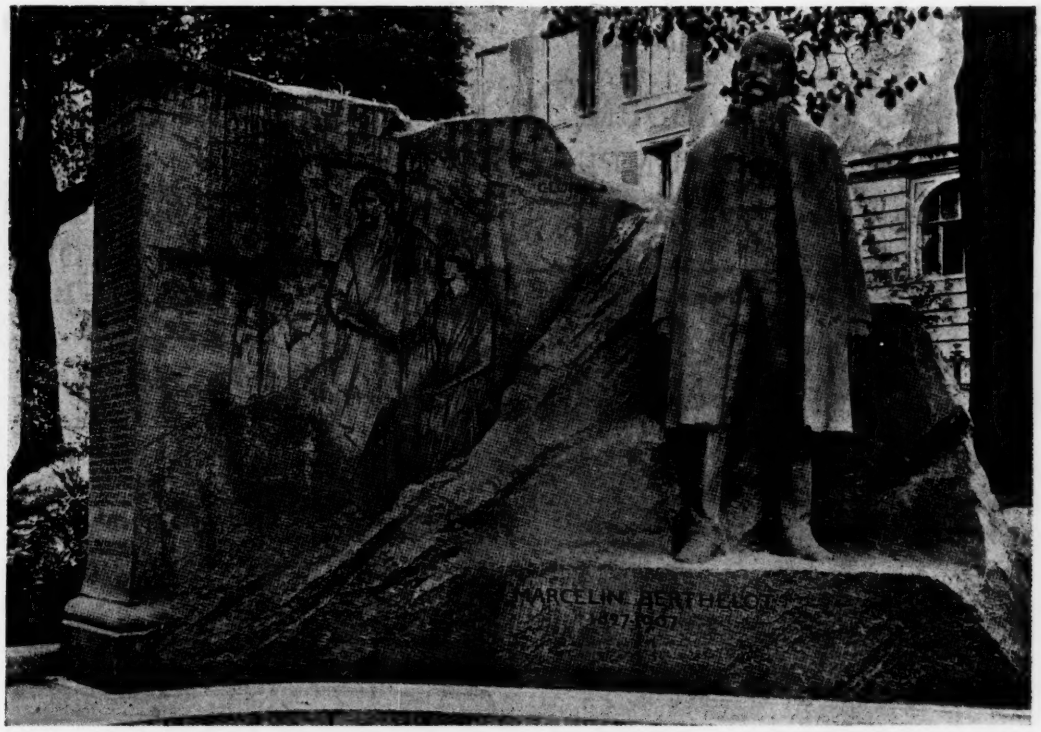

Lest We Forget

AMONG the monuments that are missing in postwar Paris is, alas, also the statue of Berthelot (designed by Saint-Marceaux) which stood in front of the Collège de France where Berthelot taught chemistry for over 40 years. As can be seen in the picture, the artist has aptly alluded to Berthelot's lifelong friendship with Renan ("Amitié"), his devotion to his wife ("Amour"), and his search for the secrets of nature which brought him lasting fame ("Gloire"). The funds for the monument, dedicated on May 20, 1917, had been secured from an international subscription. When visiting the nearby Ecole Polytechnique, one finds, however, that the statue of the student, Theunyssen, killed in the Battle of Paris (1814), and Segoffin's "Victoire," both in the courtyard of the famous school, have been preserved. Military monuments, evidently, fared better at the hands of the German invaders than those commemorating men of science!

–H. S. van Klooster

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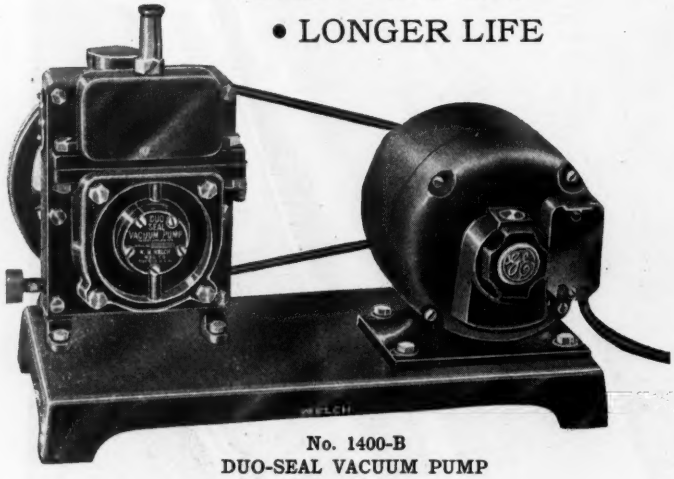

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Editor's Outlook

THE subject of the preservation of technical workers and scientists from military draft may have been worn a trifle threadbare by now, and at least may have lost some of its pressing significance. It is nevertheless a question which must be kept in mind in planning national defense for the future. It is dealt with in this connection in forceful fashion in an article in the January *Scientific Monthly*,[1] from which we quote the following:

> In event of future wars, greater care than heretofore should be given to retaining in their respective fields the largest possible number of scientific workers and students, medical students, skilled technicians, etc. The traditional dictum of our democracy that in time of war all are subject to the battle call, regardless of station, loses its validity when a literal application threatens the ability of the nation to win that battle, or to maintain its ascendency after the battle is won. Careful peacetime studies of the probable war necessity of every branch of science should be made by men qualified to judge. Likewise, ratings may be placed upon individual scientific workers on the basis of intelligence tests, college records, and subsequent work, with a view to determining degrees of dispensability in a war emergency. Similar records might be compiled to cover workers in other essential technical or professional fields requiring long periods of preparation. Consultation of these records in wartime placement of personnel would avoid unnecessary training programs and many costly delays in manning war activities.

The remainder of this article, written by a young Naval Reserve Officer, is a critical survey of some of the current proposals and contains some thoughtful suggestions on this vital topic. It follows the thesis that scientific and technical developments have made large standing armies an anachronism, explodes the current argument for compulsory military training, and calls for a redrafting of our whole educational curriculum to direct emphasis upon world problems.

The scientist certainly has his share of responsibility for the welter of confusion in the world, although not exclusive responsibility for it, as some would have us believe. The social implications of the development of nucleonic energy have already brought about the organization of groups of scientists rising to the defense of principles normally outside their own field.

Isolationism takes many strange forms, and if we are to survive we must watch that it does not hide insidiously in apparently harmless trappings.

The current plan for compulsory military training is, for example, an isolationist measure. The young men who are expected to put in a year learning the arts of soldiery are not available for military *service*, only for military *training*. Particularly are they not available for overseas service, where they are immediately needed.

If we are to discharge our international responsibilities we may need to maintain a substantial overseas force for some time to come, and if we make all our young men unavailable for this purpose under the guise of "preparedness," we may find ourselves more quickly faced with the very emergencies against which we are attempting to prepare. An *intelligently administered* Selective Service may be the right answer. It is worth thinking about.

[1] PLATT, K. B., "What is national defense?" *Sci. Mo.*, **62**, 71 (1946).

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The Semantics of Thermodynamics. Part I

W. F. LUDER

Northeastern University, Boston, Massachusetts

INTRODUCTION

SEMANTICS is the study of words and their meanings. It is such a new field of investigation that some of its cultivators may perhaps be somewhat overenthusiastic about its fertility. Nevertheless, there is good reason to suspect that the application of semantics to thermodynamics may prove illuminating.

The semanticists believe that many of the tribulations human beings bring upon themselves are due to the failure of language to communicate exact meaning. Perhaps this is nowhere more true, in science at least, than in thermodynamics. Many of the difficulties of thermodynamics might vanish if its terminology were subjected to semantic analysis.

According to the semanticists (*1*), thinking is not an independent mental process the results of which are later translated into words. Clear thinking is merely the correct use of words—based upon previous experience. If this is true, the question arises: can students be taught to think more clearly about thermodynamics through a more exact delineation of its terminology? This paper represents a tentative attempt to call attention to this question.

Probably most students have more difficulty with thermodynamics than with any other phase of their chemical training. Yet those of us who are familiar with the *language* of thermodynamics find it difficult to understand why students have so much trouble. We forget our own earlier troubles with that language. Perhaps the fundamental difficulty is really in the carelessness with which we use it. Possibly we have become too much accustomed to depending upon context for the meaning of the words we use. We are prone to forget that students do not have sufficient background to depend wholly upon context. The terms we use for the various specialized functions and operations of thermodynamics should be carefully defined and their meanings limited as definitely as possible. This alone is not sufficient, however. The use of the terms must be illustrated in ways which correspond with the student's previous experience.

To show the effect upon the uninitiated of depending too much upon context, let us consider the following sentences:

1. She can no longer wear that coat because she has grown too ——.
2. He is living off the —— of the land.
3. The —— is in the fire.

To an American it is obvious that one three-letter word will suffice for all three blanks; therefore, it is unnecessary actually to use the word in the sentence in order to convey the meaning to another American. But try the three sentences on a Russian student of the English language! He would probably use the word "large" in the first sentence, but would be baffled by the other two. The feelings of students of thermodynamics must be much the same—considering how carelessly most of us misuse the language of thermodynamics.*

Before starting upon our excursion into the semantics of thermodynamics, perhaps it would be well to lay out a map of the ground to be covered. For student chemists the most important preliminary objective is an understanding of free energy and equilibrium. It would seem that side excursions into a detailed discussion of the Carnot cycle and the so-called efficiency† of heat engines are unnecessary for chemistry students (*3*). In the following discussion we shall make an attempt to keep on the main path to the important objective.

THE FIRST LAW

Some of the terms used in the treatment of the First Law of thermodynamics are generally agreed upon, but others are still the subject of controversy. An outstanding example of this is Brönsted's criticism of classical thermodynamics (*4*). The disagreement between Brönsted and most other writers offers an apt illustration of the semanticist's explanation of many human misunderstandings. Brönsted uses the same words, but his understanding of their meanings is not that of the majority of chemists. The difference is most evident in the use of the terms "heat" and "work." (This should make students who have difficulty with the meaning of these words feel better.)

In discussing the meaning of heat and work, let us make use of mathematics since it is generally agreed upon that mathematics is of great value in expressing exact meaning. Various mathematical expressions of the First Law follow:

$$\Delta E = q - w \tag{1}$$

$$dE = d(q - w) = Dq - Dw \tag{2}$$

$$dE = Dq - p_{ext}dv - Dw' \tag{3}$$

$$dH = Dq + vdp - Dw' \tag{4}$$

Some chemists advocate depending entirely upon mathematical equations in thermodynamics; however, most of us seem to prefer to make some attempt to

* I hasten to admit my own guilt in this carelessness. Following general usage, I have not previously (*2*) distinguished carefully enough between "spontaneous change" and "irreversible process." The distinction is an important one and will be considered below.

† This is one of the words in need of semantic analysis.

understand the meaning of the symbols in terms of our previous experience. Apparently we are supported in this feeling by the semanticist. The semanticist's search for the "referent" corresponds to the scientist's attempt to base his use of abstract (even if mathematical) ideas solidly upon experimental facts.

The above equations are of doubtful value if we do not carefully define the symbols in them. Also, in order to understand them, we must agree upon what a property of the system is, the difference between "*d*" and "*D*", how equation (4) is obtained from (3), as well as the meaning of E, q, w, w', and H.

E, the "internal energy" of a system, is by definition a characteristic function, *i. e.*, a property of the system. It has an actual value in any given state of the system. Both kinetic energy of molecular agitation and electrical potential energy are involved. To be sure, only *changes* in internal energy

$$\Delta E = E_2 - E_1 \tag{5}$$

can be *measured* and only as the system changes from state one to state two. Nevertheless we find it helpful to picture the internal energy of a gas, for example, as a sum such as

$$E = E_t + E_v + E_r + E_o \tag{6}$$

where E_t is energy of translation, E_v is energy of intramolecular vibration, E_r is energy of molecular rotation, all of which may change with temperature, while E_o may be regarded as the sum of all forms of intrinsic energy which are not functions of temperature.

Now, q and w are entirely different quantities. (w. is merely all work other than pv work.) And q and w are not properties of the system. Consider two states of the simple system shown in Figure 1. The system has internal energy at each state, but there is no q or w in the system, for q and w are only observed during a change from one state to another state as they affect the surroundings. In this particular change some of the atmosphere has been moved and energy has flowed into the system. The energy required to move the atmosphere is called work. When the expansion takes place slowly and the walls of the cylinder are uninsulated, only a small temperature difference will be observed; but due to this difference, energy of kinetic agitation is transferred to the system from the surroundings. *Heat is energy transferred from one system to another solely as the result of a temperature difference.* There is no heat energy in a system! There is internal energy but not heat energy. Heat is energy being transferred. We should not speak of heat energy as if it existed in a system. To avoid confusion we should drop the use of "*thermal* agitation," because its use implies that we believe that there is actually heat in a system as such. If we decide it is a useful term, we must learn to associate "thermal" with temperature rather than with heat.

Carelessness in the use of the word "heat" is still so widespread that it seems worth while to emphasize the point by considering two different methods by which the change in Figure 1 may be carried out. These are

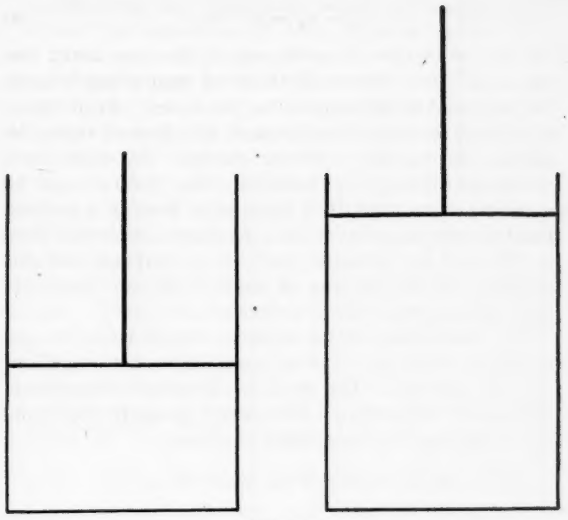


FIGURE 1

STATE 1	STATE 2
p = 4 atm.	p = 2 atm.
V = 10 l.	V = 20 l
T = 300°	T = 300°

graphed in Figure 2. The two different methods of changing from state one to state two are designated "paths *a* and *b*." Path *a* is an isothermal expansion Path *b* is carried out first at constant pressure, then adiabatically. Now

$$\Delta E_a = \Delta E_b \tag{7}$$

since we are talking about the same change; therefore from equation (1)

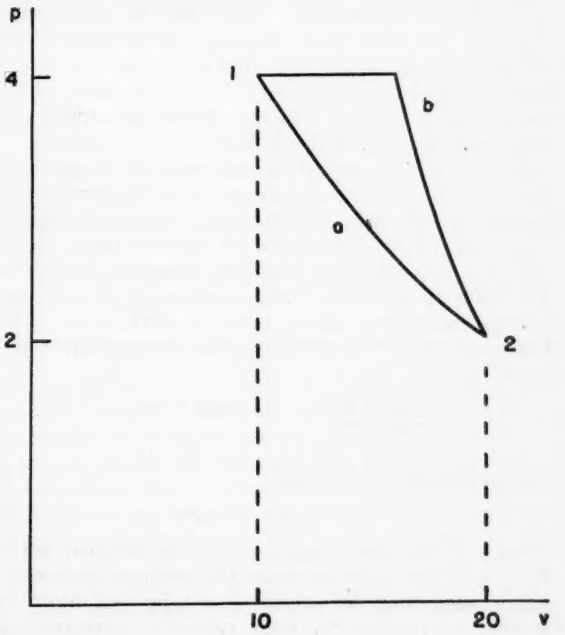


FIGURE 2

$$q_a - w_a = q_b - w_b \qquad (8)$$

but the work done in each case is the area under the curve, $\int_1^2 p dv$. Obviously the work done depends upon the path and is different in the two cases. From equation (8) it is evident that q must also depend upon the method of carrying out the change. By some such reference to simple experiments the student can be made to understand that there is no heat *in* a system. Heat is only manifest when a change is made and then is different for different methods of carrying out the change. A shorter way of saying this is: *Heat and work are not properties of a system.*

The distinction between properties of a system and quantities such as q and w is emphasized in equations (2), (3), and (4). The small "d" is used in its customary sense. Therefore it is incorrect to apply it to q and w. A capital "D" is required (*5*); i. e.,

d = a small *change in* the value of...
D = a small value of...

The integrals of Dq and Dw are q and w, not $q_2 - q_1$ or $w_2 - w_1$:

$$\int_1^2 dE = E_2 - E_1 = \Delta E$$

but

$$\int_1^2 Dq = q$$

The expression $q_2 - q_1$ (meaning Δq) is quite frequently seen in print although it has no experimental significance whatever! (One textbook actually contains the symbols Δq and Δw.) This example would delight a semanticist. It is a marvelous illustration of semantic confusion. We define q so that it *cannot* be a property of the system. Then when we are careless in using "the most exact language, mathematics," we get an expression which says that q *is* a property of the system. The use of "d" and "D" (*5*) to show which functions are properties of the system and which are not can do much to eliminate this source of confusion.

In view of the preceding discussion, it is apparent that to call H the "heat content" is particularly inappropriate. There is no such thing! Of several suggestions which have been made for another term, "total energy" (*6*) seems best from the semantic viewpoint. Equation (4) is obtained from equation (3) by a mathematical operation, adding $d(pv)$ to both sides. The left-hand side of the resulting equation is abbreviated as dH:

$$\underbrace{dE + d(pv)}_{dH} = Dq + vdp - Dw'$$

so that H may be defined as

$$H = E + pv \qquad (9)$$

Some authors believe equation (9) to be sufficient definition for H, but again we make the semantic (and scientific) point that definitions should be tied down as closely as possible to their referents (experimental basis). Suppose we rewrite equation (9) as follows

total energy = internal energy + pressure-volume energy (10)

and then try to visualize its meaning in terms of previous experience. In Figure 3 we have a mol of mercury so arranged that it can be removed from its environmental pressure (*6*). When the mercury is allowed to run down into the evacuated chamber, the piston will move down and work will be done on the system. From this picture it is obvious that every object under pressure possesses pressure-volume energy *in addition to* its internal energy.‡ "Total energy" is a logical term for this sum. Since we are only interested in changes in energy we usually deal (experimentally) with

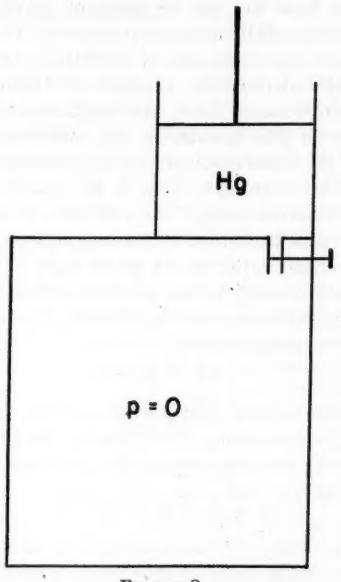


FIGURE 3

$$\Delta H = \Delta E + \Delta(pv) \qquad (11)$$

For example, when the reaction

$$C_6H_6(l) + 7\tfrac{1}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$$

takes place at 25° and 1 atm. pressure, there is a change in pv as well as in E. Since there is a decrease in volume corresponding (to a first approximation) to the disappearance of 1.5 mols of gas, $\Delta(pv) = -1.5RT$ cal.

$$\Delta(pv) = -890 \text{ cal.}$$

but

$$\Delta E = -780{,}500 \text{ cal.}$$
$$\Delta H = -781{,}390 \text{ cal.}$$

Because of the difference in pressure-volume energy, the internal energy change is different from the total energy change. When the reaction is carried out at constant pressure without any useful work being done,

‡ Other similar forms of energy may be involved, but usually may be ignored in chemical thermodynamics. Gravitational energy is one example. Chemical reactions are ordinarily carried out at a constant distance from the center of the earth; therefore, gravitational energy is constant and need not be considered.

ΔH is measured by the heat evolved, expressed by

$$\Delta H = q_p, \tag{12}$$

but this is no reason for calling H the "heat content." If the same reaction had been carried out at constant volume, the heat evolved would have measured the internal energy change:

$$\Delta E = q_v \tag{13}$$

There is no more excuse for calling H the "heat content" than there would be for giving E such a misleading name. "Heat content" is a semantic absurdity. Both from the semantic and the scientific (experimental) viewpoint, "total energy" is a better term for H.

To sum up, there is no heat as such present in any thermodynamic system. A system possesses *internal energy* and *pressure-volume energy*. The sum of the two is the *total energy*. When the state of the system is changed, the heat *transferred* from the surroundings to the system (or vice versa) may under different conditions measure either the change in internal energy, ΔE, or the change in total energy, ΔH.

The difference between q and w on the one hand and E and H on the other can be more clearly kept in mind if we are careful never to write dq and dw. Using a small "d" with q and w is a semantic absurdity, since a small "d" in mathematics always means a *small change in the value of* a characteristic function. Capital "D" to denote a *small value* of q or w should be used.

THE SECOND LAW

There are two principal semantic difficulties students encounter in most discussions of the Second Law of thermodynamics. The first is our failure to make a clear distinction between the words "change" and "process." The second is the lack of a forthright statement of the Second Law in a form which has direct bearing on the aim of chemical thermodynamics—a criterion for spontaneous changes.

The distinction between "change" and "process" may be a fine one at times; but the failure to make it is responsible for a great deal of misunderstanding of entropy, free energy, the relationship between the two, and why the chemist uses free energy rather than total entropy as a criterion of a spontaneous change. Only a few works on thermodynamics imply that any difference exists between a spontaneous change and an irreversible process; most use the terms interchangeably. This semantic confusion can lead to a number of unnecessary difficulties, a few of which will be discussed below.

Actually a given change, physical or chemical, may be carried out by an indefinitely large number of different processes. One of these is reversible and all the others involve varying degrees of irreversibility. "Process" refers to the method by which a given change is carried out. We are primarily interested in the answer to the question: Will a given chemical change (reaction) take place? So we need only consider spontaneous changes, which occur of themselves in nature.

To tie down the distinction between "change" and "process" to experimental data, suppose we consider how a spontaneous change (either physical or chemical) may be carried out by two different *methods*, one a reversible *process* and one an irreversible *process*. (The reversible process for a given spontaneous change is that method of carrying out the change which yields the maximum possible work, w_r. It is only when the maximum work is done that the change can be completely reversed without leaving any changes in the surroundings.§)

The expansion of a gas is a spontaneous physical change. This is so, regardless of the method of carrying out the change: whether by diffusion, expansion into a vacuum, or pushing against a piston to do work. The *change* may be carried out reversibly or by an indefinite number of irreversible *processes* (methods) as in Figure 4. Let us specify the spontaneous change as

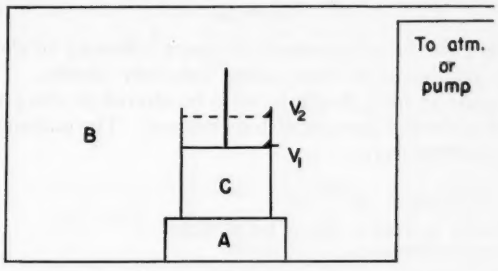


FIGURE 4

the expansion of one mol of ideal gas C at the constant temperature of 27° from a volume of $V_1 = 24.6$ l. to $V_2 = 36.0$ l. If the very large tank B is evacuated, the work done by the system when the expansion occurs is zero:

$$w = \int_1^2 p_{ext} dv = 0 \tag{14}$$

since $p_{ext} = 0$. This is the most irreversible process (method) by which the change could occur, since $w = 0$, $q = 0$ ($\Delta E = 0$ for the isothermal expansion of an ideal gas), and no heat need be supplied by the hot plate A in order to keep the temperature constant when the piston moves (assuming it to be weightless and frictionless).

Now admit air to tank B until $p_{ext} = 0.3$ atm. and repeat the change. This time

$$w = \int_1^2 p_{ext} dv = 0.3(36.0 - 24.6) = 3.42 \text{ liter-atm.} \tag{15}$$

Repeat with $p_{ext} = 0.4$ atm.; $w = 4.56$ liter-atm. At $p_{ext} = 0.5$ atm., $w = 5.70$ liter-atm. It is obvious that the greater the external pressure opposing the pressure of the gas during the expansion, the larger the amount of work which can be obtained. It should also be obvious that as p_{ext} increases, the expansion will require a longer and longer time. (The energy comes from the

§ Of course in actual practice we can never quite attain 100 per cent reversibility; but in general, we may approach reversibility so closely that the amount of work obtained is indistinguishable from w_r.

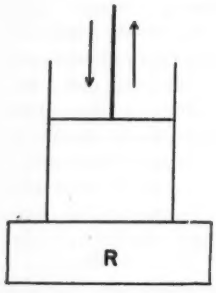


FIGURE 5

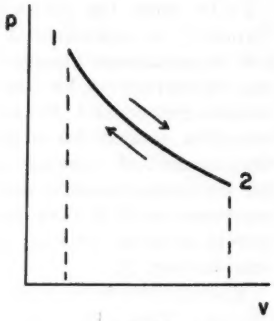


FIGURE 6

hot plate which must supply heat to the system in order to maintain constant temperature.)

To obtain the maximum work the change must be carried out so that

$$p_{gas} = p_{ext} \tag{16}$$

except for the infinitesimal difference necessary to allow the expansion to take place infinitely slowly. The pressure in tank B will have to be altered as the pressure of the gas changes with its volume. The maximum (reversible) work

$$w_r = \int_1^2 p\,dv = \int_1^2 \frac{RT}{v}\,dv$$
$$= 2.3 \times 0.082 \times 300 \times \log 36.0/24.6$$
$$= 9.36 \text{ liter-atm.} \tag{17}$$

The important aspects of the situation can be summarized as follows (t = time):

$$\text{as } p_{ext} \rightarrow p_{gas} \begin{cases} w \rightarrow w \\ t \rightarrow \infty \end{cases}$$

The closeness with which we may approach the limit—the reversible method of carrying out the change—depends largely upon our ability to wait long enough.

A concrete example such as this greatly helps to bring out the difference between "change" and "process"—the method of carrying out a given change. The spontaneous *change* considered is the same one carried out by various processes: *one* reversible and the others irreversible.

Now for an example of a spontaneous *chemical* change. It will be helpful if the analogy to the physical change just discussed is emphasized. The reaction

$$Zn + CuSO_4\ (a = 1) \rightarrow Cu + ZnSO_4\ (a = 1)$$

is a spontaneous chemical change. It may be carried out reversibly or irreversibly in a Daniell cell. The most irreversible process (method) for carrying out the change would be to short the Daniell cell terminals or to mix the reagents directly so that no work is obtained:

$$w = n\mathfrak{F}\mathcal{E} = 0 \tag{18}$$

To bring out the analogy to a gas expansion, let $\mathcal{E}$ be the back *emf* of a motor operated by the Daniell cell. Then $\mathcal{E}$ corresponds to p_{ext}. When the motor is loaded so that $\mathcal{E}$ = 0.1, 0.3, 0.6, volts, etc., in succession

w = 5107 cal. at $\mathcal{E}$ = 0.1 volt
w = 15,321 cal. at $\mathcal{E}$ = 0.3 volt
w = 30,642 cal. at $\mathcal{E}$ = 0.6 volt, etc.

The work obtainable *per mol* of zinc reacting increases as $\mathcal{E}$ increases. The time required for the reaction also increases. When the back *emf* becomes equal to $\mathcal{E}^0$ for the cell (except for an infinitesimal difference),

$$\mathcal{E} = \mathcal{E}^0 = 1.107 \text{ volts}$$

the reaction of one mol of zinc takes an infinitely long time. The maximum work per mol (assuming large enough quantities of solution so that no change in concentration occurs) is

$$w_r = n\mathfrak{F}\mathcal{E}^0 = 51{,}070 \text{ cal.} \tag{19}$$

The relevant facts can be cast into the same form as was used for the physical change:

$$\text{as } \mathcal{E} \rightarrow \mathcal{E}^0 \begin{cases} w \rightarrow w_r \\ t \rightarrow \infty \end{cases}$$

In both illustrations the distinction between the spontaneous change and the various processes (methods) by which it may be carried out is clear; however, some writers imply that the distinction between a spontaneous change and an irreversible process is an unnecessary one since it is not actually possible to realize 100 per cent reversibility in any change.‖ This is not only fuzzy thinking in itself, but can lead to real confusion when we come to the relationship between entropy and free energy. This point will be considered later.

The second of the two principal semantic difficulties students encounter in connection with the Second Law is the lack of a straightforward statement of the law in a form which has a direct application to chemical thermodynamics.

Keeping the desirability of direct application in mind, it would also seem desirable to base our statement of the Second Law as closely as possible upon the experimental facts. The Second Law thus regarded *is merely the most convenient way of summarizing the relevant facts about heat engines.* The reason why we chemists must know these facts is that they must be considered in deriving the criterion for a spontaneous change—which is what *we* are primarily interested in obtaining from thermodynamics.

The relevant facts about heat engines are as follows:

1. To be of any practical importance, heat engines must operate in cycles. Figure 5 is an illustration of the simplest kind of heat engine—a cylinder fitted with a weightless, frictionless piston and containing an ideal gas. R is a reservoir which may either supply heat to or remove heat from the gas. Allowing the gas to expand at constant temperature would result in absorption of heat from R. Work can be done as long as the expansion continues, but in practice this cannot keep up indefinitely. To continue operating, the piston

‖ Since I have been guilty of this myself (*2*), such a remark is certainly not intended as a reflection upon anyone else. I wish to express my gratitude to Professor John A. Timm for calling my attention to this semantic absurdity.

must return to its original position and repeat the cycle.

2. In order to secure any work two temperatures must be involved. If we graph the operation of the above cycle at constant temperature, we see according to Figure 6 that no more energy can be obtained from its operation than is put into it. The work done on the system to get back to *1* is the same as done by the system to get to *2*. The simplest way of operating a heat engine between two temperatures is the Carnot cycle illustrated in Figure 7. If the engine is operated reversibly the work obtained is equal to the area of the figure.

3. Only part of the heat absorbed is converted to work; some of the heat is always evolved at the lower temperature. In Figure 7, heat is absorbed at T_2 and a smaller amount is evolved at the lower T_1.

These three statements of the experimental facts are found to apply not only to the Carnot cycle, but to all other cyclic reversible heat engines. Since a law is merely a brief description of observed facts, we could regard the three statements as a preliminary form of the Second Law; however, the immediate application of the law for chemists is to the development of the concept of the free energy change *at constant temperature*. Therefore, we shall choose our wording to suit this application.

In order to do this, we note in Figure 7 that according to the First Law

$$w_r = q_2 - q_1 \qquad (20)$$

where

q_2 = heat absorbed by the engine at T_2

q_1 = heat evolved by the engine at T_1

and

$$T_2 > T_1$$

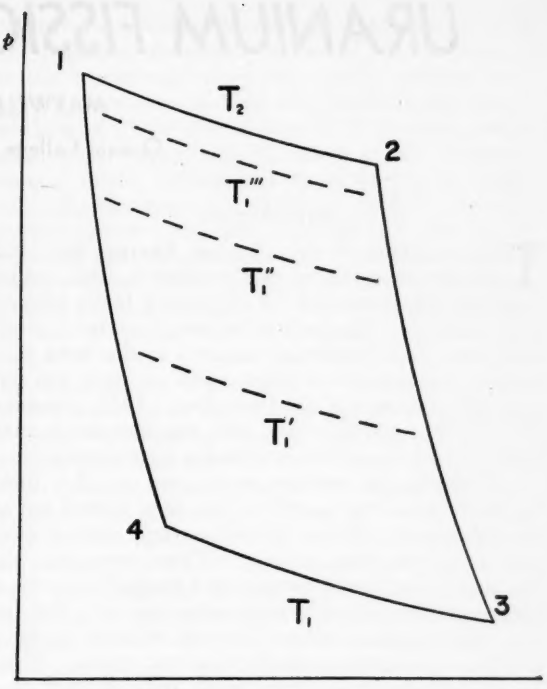
Equation (20) is true because ΔE is zero for one cycle. Referring to Figure 7, let q_2 remain constant at T_2 and observe what happens when T_1 is made to approach T_2 as indicated by the dotted lines. It is obvious that the area of the figure approaches zero as T_1 approaches T_2. Since

$$\text{area } 12341 = \int pdv = w_r \qquad (21)$$

we see that according to equation (20) q_1 approaches q_2 as w_r approaches zero.

These experimental facts are summarized in the Second Law. *The amount of work obtained from a fixed quantity of heat given up to a heat engine operating in a reversible cycle between two temperatures approaches zero as the temperature difference approaches zero.*¶

This is the form most directly applicable to the chemist's interest in thermodynamics. The pertinent facts may be indicated as follows:



Area 12341 = $\int$ pdv = w_r.

FIGURE 7

$$\text{as } T_1 \rightarrow T_2 \begin{cases} w_r \rightarrow 0 \\ q_1 \rightarrow q_2 \end{cases}$$

No further consideration of the Carnot cycle is necessary for chemists, not even to develop the concept of entropy.**

Part II will deal with semantic difficulties in the concepts of entropy and free energy.

¶ This statement of the Second Law is what all scientific laws are supposed to be: a description of directly observed facts. More "general" statements of the Second Law, such as "The entropy of the universe is continually increasing" (Clausius) or "Matter tends to concentrate; energy tends to disperse" (*7*), are too far from their semantic referrents (relevant scientific data). Furthermore, our experience is too limited to know that they actually describe experimental facts. For example, neither statement takes into account the fact that most astronomers now believe that the universe is expanding very rapidly. If this is substantiated, then the statement that matter tends to concentrate simply does not apply to the whole universe. Several textbooks include with the statement of Clausius the idea that the increasing entropy of the universe is observed at constant energy and volume. If the universe is actually expanding, the two parts of the statement are mutually contradictory. Furthermore, we now have reason to suspect that the energy of the universe is not remaining constant. Energy is being created in the stars at the expense of matter in such a way as to decrease the entropy. This will be discussed further in connection with entropy.

** It is interesting to note in passing that the so-called "efficiency" of a heat engine is another semantic absurdity. As Lewis and Randall (*8*) have pointed out, w_r/q_2 is not the efficiency, but is really the conversion factor of a perfectly efficient heat engine.

LITERATURE CITED

(1) HAYAKAWA, S. I., "Language in Action," Harcourt, Brace and Company, New York, 1942.
(2) LUDER, W. F., J. CHEM. EDUC., 21, 265 (1944).
(3) LUDER, W. F., *ibid.*, 21, 600 (1944).
(4) BRÖNSTED, J. N., *J. Phys. Chem.*, 44, 699 (1940).
(5) WOOD, S. E., J. CHEM. EDUC., 20, 80 (1943).
(6) ROSEVEARE, W. E., *ibid.*, 15, 214 (1938).
(7) FERNALD, E. M., *J. Eng. Educ.*, 50, 214 (1942).
(8) LEWIS, G. N., AND M. RANDALL, "Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1923.

URANIUM FISSION: DISCOVERIES LEADING TO A CHAIN REACTION

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INTRODUCTION

THE beginning of the "Atomic Energy Age" will probably be recorded as December 2, 1942, rather than the announced date of the atomic bomb trial on July 16, 1945. The Smyth Report (*1*) states that almost two and a half years earlier a lattice-work containing graphite and uranium metal or oxide was put together in Chicago. On December 2, 1942, this mass of material, referred to as a *pile*, was operated in such a way as to produce atomic power in a continuous manner. During the twenty years prior to this time, hundreds of nuclear reactions had been carried out in the laboratory. Many yielded several million electron volts per atom reacting. These were not self-sustaining reactions, however, and stopped as soon as the current of nuclear particles was shut off. For the first time in human history, the pile referred to above provided a continuous supply of atomic power. True, the power output was very small, only one-half of a watt at the start (*1*), but, in principle, this little pile may be the forerunner of larger structures, whose power output might compare favorably with or exceed large-scale hydroelectric power projects.

The conception of a possible chain-reacting uranium pile was introduced in 1939, soon after the discovery of uranium fission. Search along the direct lines that led to uranium fission was begun five years earlier, in 1934. The purpose of this article is to review the story of these developments up to the time that a war-secrecy blackout on publication of results in this field was imposed.

SOME FACTS ABOUT NUCLEAR PROCESSES THAT HAD BEEN ESTABLISHED BY 1934

(*a*) *Nuclear Particles.* Some of the more important particles are listed in Table 1. The masses are relative to $O^{16} = 16.00000$. Careful mass-spectrometer measurements are primarily responsible for the large number of significant figures that have been assigned. (The latter instrument is thus a far more precise tool than the atomic weight procedures that have been used by the chemist.)

TABLE 1

SOME NUCLEAR PARTICLES

Particle	*Mass*	*Charge**	*Symbols used†*
Proton	1.007589	+1	p, $_{+1}p^1$
Neutron	1.00895	0	n, $_0n^1$
Electron	0.000542	−1	e, β, $_{-1}e^0$
Positron	0.000542	+1	e^+, β^+, $_{+1}e^0$
Alpha Particle	4.003842	+2	α, $_2He^4$

* Charge is stated in electron units: 4.8022×10^{-10} e. s. u.
† Superscripts refer to mass numbers; subscripts to nuclear charge.

(*b*) *Atomic Model.* The atomic model now familiar to all students of chemistry comprises a small nucleus (approximate radius, 10^{-12} cm.) and an external electron-containing region, the effective radius of which is about 10^{-8} cm. The nucleus contains practically all of the atomic mass. It is widely accepted today that the nucleus is composed of protons and neutrons. The number of protons, or the atomic number, fixes the chemical identity of the element in question. The sum of the protons and neutrons is equal to the mass number of the element.

(*c*) *Stable Isotopes.* Many stable isotopes of the elements had been identified by mass-spectrometer experiments. The concentration of isotopes of some elements had been partially enriched by a variety of physical processes. In 1940, over 200 stable isotopes had been identified in addition to several isotopes of the naturally radioactive elements (*5*). The relative abundance of several isotopes of general interest are listed in Table 2.

TABLE 2

RELATIVE ABUNDANCE OF THE ISOTOPES OF SOME ELEMENTS

Atomic number	*Symbol*	*Mass numbers*	*Per cent abundance*
1	H	1	99.98
		2*	0.02
6	C	12	98.9
		13	1.1
8	O	16	99.76
		17	0.04
		18	0.20
17	Cl	35	75.4
		37	24.6
92	U	234†	0.005
		235†	0.71
		238†	99.28

* Commonly called deuterium.
† Naturally radioactive.

(*d*) *Artificial Radioactivity.* In January, 1934, Irene Curie and F. Joliot (*6*) reported the production of artificially radioactive elements in the laboratory. They bombarded light elements such as magnesium and aluminum with alpha particles. The sequence of reactions may be written as follows:*

$$_{13}Al^{27} + {}_2He^4 \rightarrow {}_{15}P^{30} + {}_0n^1 \qquad (1)$$

$$_{15}P^{30} \xrightarrow{t_{1/2} = 2.5 \text{ min.}} {}_{14}Si^{30} + {}_{+1}e^0 \qquad (2)$$

The phosphorus isotope produced is radioactive and decays with a half-life of 2.5 minutes by emitting a positive electron or positron. The product is a stable isotope of silicon. In the interval 1932–42, over 400 radioactive isotopes were prepared by a variety of

* Superscripts refer to mass numbers; subscripts to atomic numbers. Total mass and nuclear charge are the same for the reacting atoms and products.

nuclear reactions (*5*). Several artificially radioactive isotopes are listed in Table 3.

TABLE 3

SOME ARTIFICIALLY RADIOACTIVE ELEMENTS THAT HAVE FOUND APPLICATIONS IN OTHER FIELDS OF INVESTIGATION

Atom	*Half-life*	*Type of emission*	*Use*
C^{11}	21 minutes	Positron	Study of photosynthesis
P^{32}	14.3 days	Electron	Soil studies; leukemia treatment
Fe^{59}	47 days	Electron	Anemia studies
I^{128}	25 minutes	Electron	Thyroid studies

(*e*) *Mass-Energy.* The Einstein relationship between mass and energy had been verified by careful accounting in a variety of nuclear reactions. According to this relationship, $E = mc^2$, where E is expressed in ergs, c is the velocity of light (2.998×10^{10} cm. per sec.) and m is in grams. According to this equation, one gram mass is equivalent to an energy of 9×10^{20} ergs. This energy value is about 2×10^{13} calories. In the units of electron volts, this corresponds to about 1000 million electron volts per atomic mass unit. The bombardment of lithium with protons by Cockroft and Walton (*7*) illustrated the application of the Einstein equation:

$$ {}_3Li^7 + {}_1H^1 \rightarrow {}_2He^4 + {}_2He^4 \qquad (3) $$

The protons used had energies of 700,000 electron volts. The mass on the left side of equation (3) is 8.0241, on the right side 8.0056. The mass loss of 0.0185 mass units corresponds to 17 million electron volts using the Einstein equation. It was observed that the kinetic energy of each alpha particle was approximately 8.5 million electron volts, corresponding to a total energy of 17 million electron volts. The Einstein equation was thus verified within the experimental error of the measurements (*1*).

THE BOMBARDMENT OF URANIUM BY NEUTRONS

Not long after the discovery of the neutron in 1932, Fermi and his coworkers at the University of Rome were engaged in a systematic study of reactions of various elements with neutrons. Since neutrons have no charge and consequently are not readily repelled by external electron shells, they are readily absorbed by many target atoms. The nuclear processes were usually of the same type:

$$ {}_ZX^M + {}_0n^1 \rightarrow {}_ZX^{M+1} + \text{gamma rays} \qquad (4) $$

$$ {}_ZX^{M+1} \rightarrow {}_{Z+1}X^{M+1} + {}_{-1}\epsilon^0 \qquad (5) $$

The target atom absorbs the neutron. The isotope resulting is usually unstable and decays to the next higher element in the periodic system by emission of a beta particle. Therefore, if uranium ($Z = 92$) were made the target atom, atoms having an atomic number of 93 or higher might result by successive emissions of beta particles (*8*). This technique might thus be used to prepare transuranic elements, elements having atomic numbers greater than 92. It should be possible to establish the presence of transuranic elements in neutron-irradiated uranium by ordinary "carrier" techniques (*2*). Using the latter, it might be possible to eliminate as products known elements with $Z < 92$. Any remaining radioactivities would then be assigned to the transuranic elements. Using uranium as a target for neutrons, at least four radioactivities having half lives of 10 seconds, 40 seconds, 13 minutes, and 90 minutes were reported (*9*). Element 93, if it were present, might be expected to belong to the ${}_{25}Mn$, ${}_{43}Ma$, ${}_{75}Re$ subgroup. A portion of the activities could be precipitated along with a manganese carrier. By the end of 1934, it appeared certain that these activities were not caused by isotopes of any of the elements from radon to uranium, inclusive ($Z = 86$–92). The hypothesis was therefore made that these activities were caused by one or more of the transuranic elements. This conclusion was criticized by Noddack (*10*) who pointed out that it would be necessary to eliminate *all* known elements by "carrier" techniques before arriving at this conclusion.

Von Grosse and Agruss (*11*) in 1935 reported evidence for ${}_{91}Pa$ as one of the active products. Careful checks by d'Agostino and Segrè (*12*) and Hahn and Meitner (*13*) showed that the 13 minute and 90 minute activity could be completely separated from ${}_{91}Pa$ "carrier." As a result of the work done in 1935, there was considerable evidence to show that the 13 minute and the 90 minute activities were not isotopic with any of the known elements from $Z = 80$ to $Z = 92$ (mercury through uranium).

Meitner, Hahn, and Strassman (*14*) assigned the activities produced in neutron-irradiated uranium to transuranic elements. By studying the activities produced under various irradiation conditions, they attempted to formulate parent-daughter series that would best explain the experimental facts. In 1937, they concluded that three different radioactive isotopes of uranium were formed by neutron bombardment and that each proceeded to build up a series of transuranic products. The series extended up to *element 97*. Several aspects of this solution, however, appeared improbable to many physicists.

A new lead was uncovered by the French investigators, Curie and Savitch. In 1937–38, the latter discovered an active product from neutron-irradiated uranium that had a half-life of 3.5 hours (*15*). This product could be precipitated with lanthanum ($Z = 57$) as a carrier. Since their attention was centered on elements near uranium, they tested its behavior using actinium ($Z = 89$) as "carrier." By fractional precipitation of the oxalates from an active solution containing both lanthanum and actinium "carriers," they found that the 3.5-hour product resembled lanthanum more closely in chemical behavior. In fact, they were forced to admit that the chemical properties of this product were those of lanthanum. They were unwilling to conclude that it *was* lanthanum because they appeared to observe a slight concentration of the 3.5-hour product in the first portion of the precipitate obtained on addition of ammonia. It thus seemed necessary to allocate this product to one of the transuranic elements. It is clear today that Curie

and Savitch were on the verge of discovering uranium fission, for the 3.5-hour activity is actually caused by an isotope of lanthanum.

THE DISCOVERY OF URANIUM FISSION

The work of Curie and Savitch was repeated by other investigators. Hahn and Strassman (*16*) in 1938 found that three active products could be precipitated when barium ($Z = 56$) was used as a "carrier." They further demonstrated that these active products gave rise to three daughter elements that could be carried with lanthanum ($Z = 57$). Barium and lanthanum are 36 and 35 atomic numbers removed from uranium. As a result, their radiochemical experience led them to look for elements close to uranium that would resemble barium and lanthanum in chemical properties. They attributed the barium-carried product to radium ($Z = 88$) and the lanthanum-carried product to actinium ($Z = 89$). It was further assumed that the radium was formed from an excited ${}_{92}U^{239}$ nucleus by the emission of two alpha particles. Physicists pointed out several serious faults with the radium formation hypothesis. As a consequence, Hahn and Strassman (*17*) in 1939 improved their experimental methods in order to confirm their belief that barium-carried activities were due to *radium*. There now appeared to be four such products. The latter, called "Radium IV," had a half-life between 250 to 300 hours. Their search narrowed down to two elements, *barium* or *radium*. (It may be recalled from the pioneer work of Marie Curie that the chemical properties of barium and radium are very similar.) One of their final tests involved fractional crystallizations from a solution containing (*a*) the "Radium IV" product, (*b*) added barium "carrier," and (*c*) an isotope of radium also added as carrier. The radium isotope concentrated in the expected manner, but the "Radium IV" product remained uniformly distributed. "Radium IV" thus turned out to be an isotope of *barium*. This was a completely unexpected solution of their problem. An unusual nuclear reaction must have occurred in order that element 56 be produced from element 92. It was soon confirmed that the daughter products were actually isotopes of the next higher element, lanthanum. "Radium IV" appeared to be a barium isotope having a mass number of 140. If the original uranium atom split to give two fragments, there should be other products having a mass number of approximately 98. Radioactive strontium ($Z = 38$) and yttrium ($Z = 39$) were soon identified. An air stream bubbled through a solution of a neutron-irradiated uranium salt picked up a radioactive noble gas that proceeded to deposit a radioactive solid in a cotton filter. The gas was probably xenon ($Z = 54$) or krypton ($Z = 36$). The solid deposit contained active rubidium ($Z = 37$) or cesium ($Z = 55$) or both. There soon appeared little doubt that almost all the products resulting from the neutron bombardment of uranium belonged to elements in the middle of the periodic system and not to the transuranic elements. This splitting of uranium into two more or less equal fragments was named "*uranium fission*."

THE HIGH ENERGIES ACCOMPANYING URANIUM FISSION

The extraordinary interest attending the announcement of the discovery of uranium fission had few parallels in the annals of modern science. American scientists were informed about this discovery in January, 1939, by Professor Niels Bohr (*1*, *2*). It was immediately evident to almost all nuclear physicists that the splitting of uranium into two more or less equal fragments should be accompanied by an energy release far in excess of that liberated by common nuclear processes. The facts leading to this conclusion were based on the accumulation of accurate isotopic atomic masses by mass-spectrometer measurements. If the nucleus is composed of neutrons and protons, then simple addition of the latter masses might be expected to yield a value very close to the measured atomic mass. If this sum is greater than the measured mass, the difference would correspond to the exothermic energy liberated in the hypothetical formation of the nucleus from the constituent particles. Using a concept familiar to the chemist from consideration of ordinary chemical reactions, the binding energy (*1*) of the nucleus may be defined as:

$$\text{Binding energy} = (ZM_p + NM_n) - M_{exp} \qquad (6)$$

where Z and N are the number of protons and neutrons, respectively; M_p and M_n are the masses of the proton and neutron, and M_{exp} is the measured mass of the nucleus. The mass number, M, is defined as the total number of particles inside the nucleus and is equal to $Z + N$. The binding energy per particle (*B. E. P.*) is obtained by dividing the nuclear binding energy above by M. The (*B. E. P.*) may be considered a measure of nuclear stability.

Starting from the light nuclei, the general trend of the (*B. E. P.*) is to increase to a maximum about $M = 60$ (Fe, Co, Ni, Cu, Zn) and then to *decrease* gradually with increasing M. Hence the nuclei in the middle of the periodic table are more strongly bound than those on either side. Any process that furnishes particles in which the constituents are more firmly bound [have a greater (*B. E. P.*)] than in the original nuclei should be highly *exothermic*. This may be considered in a related manner: when a heavy nucleus (near the end of the periodic table) splits into two products of approximately equal mass, the sum of the masses of *stable* isotopes of the products is less than that of the original particle. According to Einstein's relationship, this loss in mass would appear in the form of the kinetic energy with which the fragments shoot away from the fission scene. Part of the energy might appear in the form of other high-energy particles or in gamma radiation. Given a table of (*B. E. P.*) values, the energy calculations are straightforward. Assuming that element 92 undergoes fission to give elements 54 and 38 (or other similar pairs) the energy per fission amounts to 200 million electron volts. An electron volt

per atom corresponds to 23,060 calories per gram atomic weight. The heat of formation of a mol of carbon dioxide gas from the elements is approximately 94,000 calories or about 4.1 electron volts per carbon atom. In other words, the fission of a uranium atom liberates about *50 million times* more energy than the combustion of one carbon atom.

The high energies of the fission fragments were confirmed within a few weeks by experiments reported in the leading American, British, German, and French scientific journals. In one method, a thin layer of uranium was placed inside an ionization chamber containing gas molecules. Ordinarily the alpha particles emitted by uranium cause ionization of the gas inside the chamber. This ionization current is then amplified and is observed as a series of relatively small kicks or pulses on a typical oscilloscope screen. On bringing up a source of neutrons, tremendous kicks were observed on the screen. From their size the energy of the particles that produced the ionization in the gas chamber was estimated to be of the order of one hundred million electron volts.

The Wilson cloud chamber was also used to demonstrate the existence of the high-speed fragments that resulted from uranium fission. Samples of uranium were placed inside the chamber. In the absence of a source of neutrons, cloud chamber photographs showed the weak tracks of alpha particles emitted from the uranium. When the neutron source was introduced, a large number of heavy particle tracks could be observed.

A third and ingenious method shed additional light on the nature of the fission reaction. The light fragments resulting from the uranium breakdown should have sufficient energy to tear themselves completely away from the uranium sample. In that case, it should be easily possible to catch them on a collector placed near but not necessarily touching the uranium sample. Various collecting surfaces were used, including cylinders of Bakelite, a water surface, a pad of cigarette papers, and a glass plate. In all cases, the collector surface became radioactive. Furthermore, the radioactive elements caught by the collectors were identical with those produced in the bulk of the uranium sample. The collecting surface could be placed at a reasonable distance away from the uranium, for the high-energy fission fragments could travel about an inch in air before they lost all their energy by collisions and stopped.

OTHER DISCOVERIES RELATED TO URANIUM FISSION

The discovery of uranium fission raised a great variety of associated problems. These were attacked vigorously on an international scale in 1939. Approximately 100 papers on the subject were reviewed in January, 1940, by Turner (*3*). Partial answers to several important questions were published prior to the imposition of restrictions for the sake of military security.

Fission of Other Elements. The fission of uranium by slow (thermal velocity) neutrons and fast neutrons was recognized early. Slow neutrons having a kinetic energy of the order of magnitude of gas molecules at room temperature appeared to have a greater probability of causing fission in uranium. Fast neutrons would cause fission of thorium atoms ($Z = 90$). Von Grosse, Booth, and Dunning (*18*) found that fast neutrons would induce fissions in protoactinium ($Z = 91$) but that thermal neutrons were not effective. Many other elements were bombarded with neutrons having a reasonably large range of energies. Roberts, Meyer, and Hafstad (*19*) used neutrons obtained by bombarding a lithium target with one million electron volt deuterons. These neutrons had energies up to 13.5 million electron volts. Fissions in amount greater than $^1/_{1000}$ relative to that for thorium were not found when bismuth, lead, thallium, mercury, gold, platinum, tungsten, tin, or silver was used. These elements have atomic numbers of 83 through 78, 74, 50, and 47, respectively.

The Products of Fission. The pioneer work of Hahn, Meitner, and Strassman had shown that fission products are found in the middle of the Periodic System and that many are radioactive. Simple calculations predicted that an initial pair of fission fragments would be the parents of two series of radioactive generations. The series would stop only when a stable isotope of a daughter element is formed. An example considered by Turner (*3*) well illustrates this point. Assume that a uranium nucleus having a charge of 92 and a mass number of 239 splits by fission to form ${}_{54}Xe^{140}$ and ${}_{38}Sr^{99}$. The stable isotopes of xenon range in mass number from 124 to 136 (*4*). In the case of strontium they range from 84 to 88. The ${}_{54}Xe^{140}$ isotope is unstable and will probably decay by successive beta-particle emissions to give

$$ {}_{55}Cs^{140} \rightarrow {}_{56}Ba^{140} \rightarrow {}_{57}La^{140} \rightarrow {}_{58}Ce^{140} $$

The latter isotope of cerium is known to be stable and is present to the extent of about 90 per cent in a sample of ordinary cerium. The radioactive chain would stop, therefore, with cerium. Similarly, the ${}_{38}Sr^{99}$ would decay through the sequence

$$ {}_{39}Y^{99} \rightarrow {}_{40}Zr^{99} \rightarrow {}_{41}Cb^{99} \rightarrow {}_{42}Mo^{99} \rightarrow {}_{43}Ma^{99} \rightarrow {}_{44}Ru^{99} $$

The latter isotope of ruthenium is stable and is present to the extent of about 12 per cent in a sample of ordinary ruthenium. The latter chain stops here. Turner (*3*) lists as probably or definitely identified fission products having atomic numbers 34–9, 42, 43, 47, 51–7. During 1940–41, evidence for the existence of elements 40, 41, 44, 45, 46, 48, and 49 were published in the *Physical Review*. Thus, with the exception of tin, element 50, fission products of uranium and thorium have been reported over the atomic number range 34 to 57, all the way from selenium to lanthanum. In the case of some fission elements, more than one isotope was found. At least four different radioactive isotopes of tellurium were found. It may be noted that the quantities of radioactive fission products that were handled in these investigations were usually too

small to be weighed on the most sensitive balances. Due praise should be given to the skillful labors of the chemists and physicists in this field.

The Isotope of Uranium Principally Responsible for Fission. Bohr and Wheeler (*20, 21, 22*) made pioneer contributions to the theory of nuclear fission. Their calculations indicated that a uranium-238 nucleus is not sufficiently perturbed by the entrance of a slow neutron to induce fission. However, in the case of uranium-235, they conclude that the extra energy introduced should be sufficient to permit the fission to occur. This conclusion was verified by a number of brilliant experiments. The 235 isotope is present to the extent of only 1 part in 140 in ordinary uranium. The 238 isotope is approximately 139 times as abundant while the 234 isotope is present to only a very slight extent, 0.006 per cent of the total. Minute quantities of the isotopes were separated using a mass spectrometer. The separated portions were then irradiated with thermal neutrons and a number of fissions were measured (*23, 24*). As predicted by the theoretical calculations of Bohr and Wheeler, the 235 isotope was responsible for the major portion of the fissions by slow neutrons.

Secondary Neutrons Resulting from Fission. While discussing the products of fission (above), an example in which a U^{239} atom underwent fission to produce $_{54}Xe^{140}$ and $_{38}Sr^{99}$ was considered in some detail. Both initial products were found to have a higher mass number than corresponded to their heaviest known stable isotope. In the example given, stability was finally achieved by successive beta-emissions. Alternately, the unstable isotope might eliminate some of the "excess" mass by emission of one or more neutrons. Since the latter would be produced as a result of fission, they would be called *secondary* neutrons. It was soon established that secondary neutrons were emitted during fission. This fact is of the greatest consequence to the entire subject of the *large-scale* release of atomic energy. (This will be amplified below.) Several experiments dealing with the number of secondary neutrons produced in every fission were reported in 1939. Von Halban, Joliot, and Kowarski (*25*) concluded that 3 to 4 neutrons might be produced per fission, and in another publication with Perrin (*26*) reported 3.1 secondary neutrons. Zinn and Szilard (*27*) reported 2.3 secondary neutrons per fission.

THE POSSIBLE LIBERATION OF LARGE-SCALE ATOMIC ENERGY

Were it not for the existence of the secondary neutrons, the uranium fission reaction would not have been of especial interest from the standpoint of the production of atomic energy on a large scale. This would be true even if the energy per fission had been 10,000 million electron volts instead of 200. Several elementary calculations of the energies involved will illustrate this point. Two hundred million electron volts corresponds to 8.9×10^{-18} kilowatt-hours. The complete fission of a gram of uranium atoms would liberate approximately 23,000 kilowatt hours. If no secondary neutrons were produced by fission, over 10^{21} primary neutrons would be needed. This number could be produced in the laboratory, but the time required would be unreasonably long. Further, the energy input in the experiment would far exceed the fission energy released. Thus, uranium fission would be a highly interesting nuclear process, but would have little large-scale possibilities.

As soon as the existence of secondary neutrons was confirmed, the possibility arose that a chain reaction might be produced that could yield large-scale atomic power or a catastrophic explosion. The concept of a chain reaction has been familar to chemists in connection with various rate mechanisms, including the photochemical combination of chlorine and hydrogen and the explosion of hydrogen-oxygen mixtures. In the case of uranium fission, the chain carriers would be these secondary neutrons. A controlled chain reaction would imply a reasonably constant neutron density. If the neutron density were permitted to increase exponentially, a violent reaction would probably occur (*1, 2, 3*).

A hypothetical example may be used to illustrate the latter statement. Assume (*a*) that every fission gives rise to two secondary neutrons, (*b*) that each secondary neutron will induce fission in a uranium atom, and (*c*) that the lifetime of a secondary neutron is one-thousandth of a second. Each fission gives rise to 200 million electron volts of energy. The number of fissions per second will rise in an exponential manner, doubling for every 0.001 second. In one-tenth of a second, over 10^{30} fissions would be taking place, furnishing more energy (unfortunately almost all in the form of heat) than the TVA development. The latter example leads, of course, to a ridiculously high figure.

Flugge (*28*) estimated that should the chain reaction be possible, one cubic meter of U_3O_8 would develop about 10^{12} kilowatt-hours in less than one-hundredth of a second.

Effective Secondary Neutrons. The production of more than one secondary neutron per fission is not sufficient, however, to make a chain reaction possible. The critical fact needed is, of course, the number of secondary neutrons that are able to induce new fissions in U-235 atoms. In other words, the number of *effective* secondary neutrons must be greater than one. It was recognized in 1939 that a secondary neutron could become useless to the chain reaction in at least three ways:

1. The secondary neutron might simply escape from the uranium mass before undergoing a nuclear reaction.

2. The secondary neutron might be absorbed by a uranium-238 atom without leading to fission. The process might be written:

$$_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239}$$

$$_{92}U^{239} \xrightarrow{t_{1/2} = 23 \text{ min.}} {}_{93}(93)^{239} + {}_{-1}\epsilon^{0} \qquad (7)$$

Since over 99 per cent of the uranium consisted of this isotope, it was clear that this capture process might seriously decrease the chances for a chain reaction.

3. The secondary neutrons might be absorbed by impurities present in the uranium used.

Various suggestions were considered in 1939 (*3*) in order to minimize the effects listed above. The possibility of neutron escape could be minimized by making the dimensions of the uranium-containing mass larger. Methods of slowing down the secondary neutrons efficiently were also considered, for it was observed that the probability of uranium-235 fission was greater when irradiated with slow neutrons (*3*). Neutrons may lose energy and become slowed down to thermal velocities by making elastic collisions with other particles. In general, the exchange of energy is most efficient when the colliding particles have approximately the same mass. For this reason, hydrogen containing substances such as water were considered in this connection. Unfortunately, it appeared that the material used to slow down the neutrons might also capture an excessive number. *Not enough* data were available at the end of 1939 to warrant the conclusion that a chain reaction with *ordinary* uranium was possible (*29*, *30*).

With the publication of the Smyth Report (*1*) it is possible to obtain a limited view of the developments in this field during the years 1940 to 1945. On December 2, 1942, a chain reaction was maintained in a pile that contained lumps of uranium metal or oxide regularly spaced throughout the neutron "slow-downer" material, graphite. According to this report, this was the first chain-reacting uranium fission "engine" in human history.

LITERATURE CITED

(1) SMYTH, H. D., "Atomic Energy for Military Purposes," Princeton University Press, Princeton, **1945.**

(2) POLLARD, E., and W. L. DAVIDSON, "Applied Nuclear Physics," John Wiley and Sons, Inc., New York, **1942.**

(3) TURNER, L. A., "Nuclear fission," *Rev. Modern Phys.*, **12,** 1–29 (1940).

(4) TAYLOR, H. S., AND S. GLASSTONE, Editors, "Treatise on Physical Chemistry" Volume I, D. Van Nostrand Company, New York, **1942,** Chapter I.

(5) LIVINGOOD, J. J., AND G. T. SEABORG, *Rev. Modern Phys.*, **12,** 30 (1940). This reference contains tables listing both stable and artificially radioactive isotopes.

(6) CURIE, I., AND F. JOLIOT, *Compt. rend.*, **198,** 254 (1934).

(7) COCKROFT, J. C., AND E. T. S. WALTON, *Proc. Roy. Soc. London*, **A136,** 619 (1932); **A137,** 229 (1932).

(8) FERMI, E., *Nature*, **133,** 898 (1934).

(9) AMALDI, E., O. D'AGOSTINO, F. RASETTI, AND E. SEGRÈ, *Proc. Roy. Soc. London*, **A146,** 483 (1934).

(10) NODDACK, I., *Z. angew. Chem.*, **37,** 653 (1934).

(11) VON GROSSE, A., AND M. S. AGRUSS, *J. Am. Chem. Soc.*, **57,** 438 (1935).

(12) D'AGOSTINO, O., AND E. SEGRÈ, *Gazz. chim. ital.*, **65,** 1088 (1935).

(13) HAHN, O., AND L. MEITNER, *Naturwissenschaften*, **23,** 37, 230 (1935).

(14) MEITNER, L., O. HAHN, AND F. STRASSMAN, *Z. Physik*, **106,** 249 (1937).

(15) CURIE, I., AND P. SAVITCH, *J. phys. radium*, **8,** 385 (1937); **9,** 355 (1938).

(16) HAHN, O., AND F. STRASSMAN, *Naturwissenschaften*, **26,** 755 (1938).

(17) HAHN, O., AND F. STRASSMAN, *ibid.*, **27,** 11 (1939).

(18) VON GROSSE, A., E. T. BOOTH, AND J. R. DUNNING, *Phys. Rev.*, **56,** 382 (1939).

(19) ROBERTS, R. B., R. C. MEYER, AND L. R. HAFSTAD, *ibid.*, **55,** 416 (1939).

(20) BOHR, N., *Nature*, **143,** 330 (1939).

(21) BOHR, N., *Phys. Rev.*, **55,** 418 (1939).

(22) BOHR, N., AND J. A. WHEELER, *ibid.*, **56,** 426 (1939).

(23) NIER, A. O., E. T. BOOTH, J. R. DUNNING, AND A. VON GROSSE, *ibid.*, **57,** 546, 748 (1940).

(24) KINGDON, K. H., H. C. POLLACK, E. T. BOOTH, AND J. R. DUNNING, *ibid.*, **57,** 749 (1940).

(25) VON HALBAN, H., F. JOLIOT, AND L. KOWARSKI, *Nature*, **143,** 471, 680, 939 (1939).

(26) VON HALBAN, H., F. JOLIOT, L. KOWARSKI, AND F. PERRIN, *J. phys. radium*, **10,** 428 (1939).

(27) ZINN, W. H., AND L. SZILARD, *Phys. Rev.*, **55,** 799 (1939).

(28) FLUGGE, S., *Naturwissenschaften*, **27,** 402 (1939).

(29) ANDERSON, H. L., E. FERMI, AND L. SZILARD, *Phys. Rev.*, **56,** 284 (1939).

(30) TURNER, L. A., *Phys. Rev.*, **57,** 334 (1940).

Why Editors Get Gray

Mr. Gregg's article on p. 548 of the Nov. issue of the J. OF CHEM. ED. one of the sloppiest and inaccurate (sic.) articles I have ever read in a journal. The article is simply full of errors and misconceptions. How did it ever get passed (sic.) your office?

A WANING SUBSCRIBER

I should like to ask permission to reprint the article "A Simplified Electronic Interpretation of Oxidation-Reduction for Use in Teaching Organic Chemistry" by Donald C. Gregg, which appears in the November, 1945, issue of the JOURNAL OF CHEMICAL EDUCATION, Volume 22, No. 11.

I am writing a book on the training of Professional Service Representatives in the Pharmaceutical Industry and should like to use the above-mentioned article as a chapter in the book, following a chapter on chemical nomenclature....

(A READER)

THE QUALITATIVE ANALYSIS OF GROUP III

A Survey

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FOR the analysis of cations, so-called "dry methods" and "wet methods" are offered. Complete systems of analysis based either on chemical or on physical reactions are available in both the dry and wet technique. (See Bibliography, *1* to *37*) The exclusive use of some of these systems for elementary education in qualitative analysis is impractical because they offer little attraction from the educational point of view. This would be true, for instance, of the exclusive use of physical methods since the typical chemical reactions of cations are not involved. The beginners in qualitative analysis, therefore, receive instruction mainly in chemical methods of analysis (*i. e.*, the precipitation method) and since the instruction in analytical chemistry precedes the study of organic compounds, inorganic reagents are preferred. The increasing practical importance of some of the other techniques, however, makes it highly desirable to familiarize the students with at least a limited number of their applications, especially spectroscopic technique (*3* to *7*), spot tests (*8* to *12*), and some of the special organic reagents (*38* to *52*).

The systems of qualitative analysis by precipitation can be classified in two groups: those avoiding the use of sulfide ion (*14* to *25*), and the almost universally taught method of qualitative analysis, precipitation with sulfide ion. This latter system divides the cations into four or five precipitable groups and one soluble group. The consecutive precipitating agents for these groups are HCl, H_2S, and then either NH_4OH followed by $(NH_4)_2S$, or NH_4OH and H_2S used simultaneously, and finally $(NH_4)_2CO_3$. The ions of the soluble group are determined by individual reactions only.

Very little variation in the methods of qualitative determination of the HCl and H_2S group can be found, or seems to be possible, but a variety of procedures to determine the ions of analytical Group III (Al^{+++}, Cr^{+++}, Fe^{+++}, Co^{++}, Ni^{++}, Zn^{++}, and Mn^{++}) has been proposed. Generally college textbooks offer only one of these possible methods. It is the purpose of this paper and its bibliography to draw attention to the different methods available. The bibliography includes references to the systems of qualitative determinations of cations in general (*1* to *37*), qualitative analysis of Group III, and special reactions of the seven ions of this group (*38* to *82*).

We have undertaken to ask some of the authors of widely used textbooks about the special advantages of the method outlined by them and have inquired as to whether or not they think that their particular method is superior to any other.

Schematic tables of the methods given in the respective textbooks are presented below, while procedures used in the presence of interfering ions (*i. e.*, $PO_4^{\equiv}$, $C_2O_4^{=}$) have been avoided purposely. Compounds, complex salts, etc., are given as found in the denoted texts. We have included in this survey twelve textbooks (*26* to *37*) and have arranged the material in six main divisions according to the first step in the analysis of Group III:

A. CoS and NiS separated first.
B. $FeCl_3$ separated with ether.
C. AlO_2^-, $ZnO_2^=$, and $CrO_4^=$, separated first.
D. ZnS precipitated from weakly acid solution.
E. MnO_2 separated first.
F. Precipitation with NH_4OH in H_2S-free solution, followed by precipitation of filtrate with $(NH_4)_2S$.

A. CoS and NiS separated first: The fact that CoS and NiS are insoluble in dilute acids which dissolve the sulfides or hydroxides of the other ions of Group III is mentioned by Muspratt (*53*), and an intensive study has been carried out by Thiel (*54*). The textbooks of Heisig (*26*), Meldrum (*27*), Treadwell-Hall (until 1936) (*28*), and Vosburgh (*29*) use this relative insolubility of CoS and NiS as the first step for the qualitative separation of the ions of Group III. Each of these authors, however, uses variations for the determination of the five remaining ions of the group. As a second step, for instance, Heisig and Meldrum separate $Zn(NH_3)_4^{++}$, whereas Treadwell-Hall precipitate Fe^{+++}, Cr^{+++}, and Mn^{++} as hydroxides in an alkaline solution buffered by $BaCO_3$, and Vosburgh precipitates Fe^{+++}, Al^{+++}, and Cr^{+++} in ammoniacal solution. These procedures are given schematically in the attached tables.

G. B. HEISIG, "Semi-micro Qualitative Analysis," W. B. Saunders Company, New York, 1943:

... The chief merit of the analytical procedures used to separate and to identify the cations of Group III, used in my book, is that they work well in the hands of beginning students. By separating the rest of the cations from the zinc ion at the beginning of the analysis of the group, the student is not as apt to lose the zinc as when the other cations of the group are successively precipitated from the solution containing the zinc ions. The oxidation of the manganous ion by a solution of sodium bromate in sulfuric acid works well and replaces the use of a boiling mixture of concentrated nitric acid and sodium or potassium chlorate. . .

G. B. HEISIG

UNIVERSITY OF MINNESOTA

CoS, NiS, ZnS, MnS, FeS, $Al(OH)_3$, $Cr(OH)_3$ precipitated.
Add 1 *N* HCl.

Precipitate: CoS, NiS. Dissolve in conc. HCl and conc. HNO_3. Filter and boil. Neutralize with NH_4OH.

Test one part with dimethyl glyoxime for Ni^{++}.

Test another part with NH_4SCN for Co^{++}.

Solution: Zn^{++}, Mn^{++}, Fe^{++}, Al^{+++}, Cr^{+++}. Boil off H_2S. Add HNO_3, boil. Make alkaline with NH_3. Add $(NH_4)_2CO_3$. Heat.

Filtrate: $Zn(NH_3)_4^{++}$ Acidify with HAc. Add H_2S to form ZnS, soluble in HCl.

Precipitate: $MnCO_3$, $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$. Dissolve in the minimum amount of HCl. Make alkaline with NaOH, add H_2O_2. Heat. Filter.

Precipitate: $MnO(OH)_2$, $Fe(OH)_3$. Add H_2SO_4, heat, filter. Add $NaBrO_3$. Boil.

Solution: $Al(OH)_4^-$, $CrO_4^=$. Add HNO_3, then NH_3, until alkaline.

Precipitate: $MnO(OH)_2$, MnO_2. Confirm by Na_2CO_3, KClO, or by oxidation to MnO_4^-.

Solution: Fe^{+++}. Add NH_3.
Precipitate: $Fe(OH)_3$

Precipitate: $Al(OH)_3$. Confirm by Co-aluminate test or aluminon test.

Filtrate: $CrO_4^=$. Add NH_4Ac, HAc, and $PbAc_2$.
Precipitate: $PbCrO_4$.

W. B. MELDRUM, E. W. FLOSDORF, AND A. F. DAGGETT, "Semi-micro Qualitative Analysis," American Book Company, New York, **1939:**

. . . At present a revised procedure for Group III is in the process of being tested. The principal trouble experienced in our earlier Group III procedure (represented below) arose from the use of cold 1 *N* HCl for the separation of CoS and NiS from the other members of the group. An imperfect separation usually caused an interference with the confirmatory test for zinc.

While our revised procedure eliminates this difficulty entirely, since it is still in the testing stage, I prefer to make no definite statements regarding it at present. . . .

A. F. DAGGETT

UNIVERSITY OF NEW HAMPSHIRE

CoS, NiS, ZnS, $Al(OH)_3$, $Cr(OH)_3$, MnS, FeS precipitated. Make just acidic with HCl.

Residue: CoS, NiS. Dissolve in aqua regia. Test one portion for Ni^{++} with dimethylglyoxime and the other for Co^{++} with α-nitroso-β-naphthol.

Solution: Zn^{++}, Al^{+++}, Cr^{+++}, Mn^{++}, Fe^{++}. Remove H_2S, add NH_4OH and $(NH_4)_2CO_3$.

Solution: $Zn(NH_3)_4^{++}$. Confirm in HAc solution with H_2S. ZnS soluble in HCl, and in strongly ammoniacal solution. Resorcinol gives deep blue color.

Precipitate: $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$, $MnCO_3$. Dissolve in HCl, add NaOH.

Solution: AlO_3^-. Add HCl. Confirm with aluminon.

Precipitate: $Cr(OH)_3$, $Mn(OH)_2$, $Fe(OH)_3$. Treat with Na_2O_2.

Solution: $CrO_4^=$. Confirm as $PbCrO_4$ in HAc and NH_4Ac.

Precipitate: $MnO(OH)_2$, $Fe(OH)_3$. Treat with HNO_3 and $KClO_3$.

Precipitate: MnO_2. Dissolve in HNO_3 and H_2O_2. Confirm as MnO_4^- with $NaBiO_3$.

Solution: Test one portion for Fe^{+++} with NH_4OH in excess. Confirm as Prussian blue.

F. P. TREADWELL AND W. T. HALL, "Analytical Chemistry: Qualitative Analysis," John Wiley and Sons, Inc., New York, **1903:**

. . . Prior to 1914, we used the $BaCO_3$ method at the Massachusetts Institute of Technology but I don't believe any of us would go back to it. . .

W. T. HALL

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

CoS, NiS, ZnS, MnS, $Al(OH)_3$, FeS, $Cr(OH)_3$.
Treat with 2 *N* HCl.

Residue: CoS and NiS. Dissolve in HNO_3—HCl. Evaporate to dryness. Divide.

Residue: $CoCl_2$, $NiCl_2$. Dissolve in KNO_2 solution.

Precipitate: $K_3Co(NO_2)_6$.

Residue: $CoCl_2$, $NiCl_2$. Dissolve in H_2O, KCN, NaOH. Add Cl_2 gas.
Precipitate (black): $Ni(OH)_3$.

Solution: Zn^{++}, Mn^{++}, Al^{+++}, Fe^{++}, Cr^{+++}. Boil H_2S off. Add Br_2-water, boil excess Br_2 off, neutralize, and add $BaCO_3$ suspension.

Solution: Zn^{++}, Mn^{++}, Ba^{++}. Add H_2SO_4, boil, filter. Add excess of NaOH.

Residue: $Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$, $BaCO_3$. Dissolve in HCl, add H_2SO_4, filter $BaSO_4$ off. Divide:

Solution: ZnO_2^{++}. Acidify with HAc Add H_2S.
Precipitate: ZnS.

Residue: $Mn(OH)_2$. Dissolve in HCl. Neutralize with NH_3, add KCN, $(NH_4)_2S$.
Precipitate (pink): MnS.

Solution: Al^{+++}, Fe^{+++}, Cr^{+++}. Add $K_4Fe(CN)_6$.
Precipitate: Prussian Blue.

Solution: Al^{+++}, Fe^{+++}, Cr^{+++}. Add an excess of KOH. Add $KMnO_4$. Boil, filter, acidify with H_2SO_4, decolorize with C_2H_5OH. Make alkaline with NH_3.

Residue: $Al(OH)_3$.

Solution: $CrO_4^=$. Identify as blue perchromate or $PbCrO_4$.

W. C. VOSBURGH, "Introductory Qualitative Analysis," The Macmillan Company, New York, **1938:**

. . . The method of analysis of Group III in my book is the method devised by Sneed, Heisig, and Trovatten and published in the JOURNAL OF CHEMICAL EDUCATION, Vol. 5, page 87 (1928), with some minor variations. The originators of the method discuss its advantages. One important improvement, I believe, is the use of bromine rather than nitric acid to oxidize iron. Excess nitric acid introduced at that point may lead to a precipitate of sulfur in the final test for zinc, while excess bromine can be removed by boiling. Another important improvement is the slow precipitation of the hydroxides to avoid the carrying down of divalent metal ions that should remain in solution.

I selected this method for my book because it seemed simpler and better adapted to the needs of beginning students than the Noyes procedure. When the objective is to teach chemistry, a more complicated procedure capable of giving fine analytical results may be less desirable than a procedure the students can understand and follow correctly without too much practice. Materials for analysis can be adjusted to the procedure. For the same reason I do not like organic reagents; most of my students have not studied organic chemistry . . .

W. C. VOSBURGH

DUKE UNIVERSITY

NiS, CoS, FeS, ZnS, $Al(OH)_3$, MnS, $Cr(OH)_3$ precipitated. Treat with 2 *M* HCl.

Residue: NiS, CoS. Dissolve in HCl and HNO_3, heat, dilute, neutralize with NH_4OH, add dimethylglyoxime.

Precipitate: Ni-dimethyl glyoxime.

Solution: Add HAc, NH_4Ac, nitroso-R-salt conc. HNO_3.
Red solution: Co^{++}.

Filtrate: Zn^{++}, Mn^{++}, Fe^{++}, Al^{+++}, Cr^{+++}. Boil, add Br_2 (sat.) and 6 *M* NH_4OH.

Precipitate: $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$. Add H_2O, NaOH, Na_2O_2. Boil.

Precipitate: MnO_2, $Fe(OH)_3$. Add HNO_3, $KClO_3$.

Solution: AlO_3^-, CrO_4-. Add HCl, NH_4OH.

Precipitate: MnO_2. Add HNO_3, H_2O_2, $NaBiO_3$.
Pink solution: MnO_4^-.

Solution: Add NH_4OH.
Precipitate: $Fe(OH)_3$.

Precipitate: $Al(OH)_3$. Add HCl, NH_4Ac, aluminon, NH_4OH, $(NH_4)_2CO_3$.
Precipitate: Al-lake.

Solution: $CrO_4^=$. Add HAc, $Pb(NO_3)_2$.
Precipitate: $PbCrO_4$.

Filtrate: Mn^{++}, Zn^{++}. Add $(NH_4)_2CO_3$.

Precipitate: $MnCO_3$, combine with $Fe(OH)_3$ $Al(OH)_3$, $Cr(OH)_3$.

Filtrate: $Zn(NH_3)_4^{++}$. Evaporate. Add HAc, H_2S. Filter ZnS off. Dissolve in HNO_3, add NH_4OH, HAc, $CuSO_4$, (NH_4)-Hg(CNS)$_4$.
Violet precipitate: $ZnHg(CNS)_4$.

B. $FeCl_3$ separated with ether: The fact that Fe^{+++} can be quantitatively extracted from 6 *N* HCl by ether is utilized by Swift (*30*) and Noyes-Swift (*31*). Swift goes on to precipitate the sulfides of Zn^{++}, Co^{++}, and Ni^{++} by H_2S from a solution containing ammonium oxalate and sodium bicarbonate, whereas Noyes-Swift separate MnO_2 as the next step ($KClO_3$-HNO_3) and from there on follow the Noyes method (*32*) for the separation of the insoluble $Ni(OH)_2$ and Co_2O_3 from AlO_2^-, $CrO_4^=$, and $ZnO_2^=$ ions which form in very strong alkaline solutions.

E. H. SWIFT, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, **1939:**

. . . My interest was in the development of a system of analysis which would give much more quantitative separations than those provided in conventional systems. Therefore there was justification for using procedures which are not as simple as the more conventional ones. This would apply especially to the ether separation of iron, the separation of the zinc and aluminum groups, the nickel and cobalt separation, methods which are to be used only when the elements involved are present in substantial amounts and quantitative information is desired. . .

E. H. SWIFT

CALIFORNIA INSTITUTE OF TECHNOLOGY

<table>
<tr><td colspan="6">$Al(OH)_3$, $Cr(OH)_3$, FeS, ZnS, NiS, CoS, MnS. Dissolve in 6 N HCl, add Br_2, boil. Shake with ether.</td></tr>
<tr><td>Ether solution: $FeCl_3$. Evaporate. Add HCl, KI. Titrate with $Na_2S_2O_3$. Compute Fe^{+++}.</td><td colspan="5">Aqueous solution: Al^{+++}, Cr^{+++}, Zn^{++}, Co^{++}, Ni^{++}, Mn^{++}. Neutralize with NH_4OH, acidify with HCl. Add $(NH_4)_2C_2O_4$, $NaHCO_3$, H_2S.</td></tr>
<tr><td></td><td colspan="3">Precipitate: ZnS, CoS, NiS. Dissolve in HCl–HNO_3, fume with conc. H_2SO_4, dilute, neutralize with NaOH, add dil. H_2SO_4, H_2S.</td><td colspan="2">Filtrate: $Al(C_2O_4)_3^{---}$, $Cr(C_2O_4)^{---}$, $Mn(C_2O_4)_2^=$. Acidify with HNO_3, heat, evaporate, add HNO_3, evaporate, add HNO_3, $KClO_4$, heat.</td></tr>
<tr><td></td><td>Precipitate: ZnS. Add to $Fe_2(SO_4)_3$ heat. Add H_2SO_4 (precipitate: S). Solution: Zn^{++} and Fe^{++}. Titrate Fe^{++} with $KMnO_4$. Compute Zn^{++}.</td><td colspan="2">Solution: Ni^{++}, Co^{++}. Boil, add excess NaOH [precipitate: $Ni(OH)_2$, $Co(OH)_2$]. Add excess Na_2O_2. Dissolve [precipitate $Ni(OH)_2$, Co_2O_3] in HCl, evaporate, add ether. Saturate with HCl gas.
Precipitate: $NiCl_2$. Dissolve in H_2O, add NH_4Cl, NH_4OH, $AgNO_3$, KI. Titrate with KCN. Compute Ni^{++}.
Solution: H_2CoCl_4. Neutralize, add $NaBO_3$, boil, add HCl, KI. Titrate with $Na_2S_2O_3$. Compute Co^{++}.</td><td>Precipitate: MnO_2. Dissolve in HCl, KI. Titrate with $Na_2S_2O_3$. Compute Mn^{++}.</td><td>Solution: Al^{+++}, $Cr_2O_7^=$. Neutralize with NH_4OH.
Precipitate: $Al(OH)_3$ Heat and weigh. Compute Al^{+++}.
Solution: $CrO_4^=$ Acidify with H_2SO_4, KI. Titrate with $Na_2S_2O_3$. Compute Cr^{+++}.</td></tr>
</table>

A. A. NOYES AND E. H. SWIFT, "Qualitative Chemical Analysis," The Macmillan Company, New York, **1942:**

. . . In the revision of the Noyes system more conventional methods are used. . .

E. H. SWIFT

CALIFORNIA INSTITUTE OF TECHNOLOGY

<table>
<tr><td colspan="6">$Al(OH)_3$, $Cr(OH)_3$, FeS, NiS, CoS, ZnS, MnS. Dissolve in HCl, $KBrO_3$ (or Br_2), boil, shake with ether.</td></tr>
<tr><td>Ether phase: $HFeCl_4$. Shake with H_2O, add NH_4OH to aqueous phase. Precipitate: $Fe(OH)_3$.</td><td colspan="5">Aqueous phase: Al^{+++}, Cr^{+++}, Ni^{++}, Co^{++}, Zn^{++}, Mn^{++}. Evaporate. Add HNO_3, $KClO_3$, heat.</td></tr>
<tr><td>Precipitate: MnO_2. Dissolve in HNO_3, H_2O_2. Add $NaBiO_3$. Purple color: MnO_4^-.</td><td colspan="4">Filtrate: Al^{+++}, Cr^{+++}, Ni^{++}, Co^{++}, Zn^{++}. Add NaOH, Na_2O_2, Na_2CO_3.</td><td>Filtrate: $Al(OH)_4^-$, $Zn(OH)_4^=$, $CrO_4^=$. Acidify with HCl, neutralize with NH_4OH.</td></tr>
<tr><td></td><td colspan="3">Precipitate: $Ni(OH)_2$, Co_2O_3 [$Fe(OH)_3$ if not extracted previously, $Zn(OH)_2$ if 1 g. amts. of Ni^{++} or Co^{++}]. Dissolve in HCl, evaporate, add solid NH_4Cl, NH_4OH.</td><td>Precipitate: Al-$(OH)_3$. Confirm with aluminon.</td><td colspan="2">Filtrate: Zn^{++}, $CrO_4^=$. Add Na_2CO_3, boil.
Precipitate: $ZnCO_3$,$Zn(OH)_2$. Dissolve in HCl, add NH_4OH, H_2S. Precipitate: ZnS.
Filtrate: $CrO_4^=$. Add HAc, $PbAc_2$. Precipitate: $PbCrO_4$.</td></tr>
<tr><td></td><td>Precipitate: $Fe(OH)_3$.</td><td colspan="2">Filtrate: $Ni(NH_3)_6^{++}$, $Co(NH_3)_6^{++}$, $Zn(NH_3)_4^{++}$. Treat with H_2S, filter. Treat with 1 N HCl.</td><td colspan="2"></td></tr>
<tr><td></td><td>Residue: CoS, NiS. Dissolve with HCl, $KClO_3$. Evaporate, add HAc, KNO_2. Precipitate: $K_3Co(NO_2)_6$.</td><td colspan="2">Filtrate: Zn^{++}, Co^{++}, Ni^{++}. Add NaOH, Na_2O_2.
Precipitate: Ni-$(OH)_3$, Co_2O_3.
Filtrate: Zn-$(OH)_4^=$. Treat with H_2S. Precipitate: ZnS.</td><td colspan="2"></td></tr>
</table>

C. AlO_2^-, $ZnO_2^=$, and $CrO_4^=$ separated first: A widely used method of separation is based upon the fact that strongest oxidative alkaline solutions precipitate Fe^{+++}, CO^{++}, Ni^{++} as hydroxides and Mn^{++} as MnO_2 or $Mn(OH)_2$ while AlO_2^-, $CrO_4^=$, and $ZnO_2^=$ remain in solution. This method is usually called the "Noyes Method" and is used without variation (save for confirmatory tests) in the textbooks of Noyes (*32*,) Treadwell-Hall, 9th Ed. (*28*), and Reedy (*33*).

A. A. NOYES, "Qualitative Chemical Analysis," The Macmillan Company, New York, **1932:**

. . . A. A. Noyes had an ideal of getting out a scheme of analysis which would serve to detect one milligram of an element in the presence of 500 milligrams of any other. Noyes and his students worked on the scheme, which was meant to include all elements, for 30 years and regarded it as the best thing he ever did. I had Noyes as a teacher in 1894–95 and he was one of the most inspiring teachers I ever had. . .

W. T. HALL

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

<table>
<tr><td colspan="6">$Al(OH)_3$, $Cr(OH)_3$, FeS, ZnS, MnS, CoS, NiS. Dissolve in HCl, $KClO_3$, add NaOH.</td></tr>
<tr><td colspan="3">Precipitate: $Fe(OH)_3$, $Mn(OH)_2$, $Co(OH)_3$, $Ni(OH)_3$, $Zn(OH)_2$. Treat with HNO_3, $KClO_3$.</td><td colspan="3">Solution: AlO_2^-, $ZnO_2^=$, $CrO_4^=$. Acidify with HCl, add NH_4OH.</td></tr>
<tr><td>Precipitate: MnO_2. Add HNO_3, H_2O_2, $NaBiO_3$. Purple color, MnO_4^-.</td><td>Solution: Fe^{+++}, Zn^{++}, Co^{++}, Ni^{++}. Divide:
Solution: Add $K_4Fe(CN)_6$. Blue precipitate: $Fe_4[Fe(CN)_6]_3$.</td><td>Solution: Add NH_4OH, H_2S. Precipitate: ZnS, CoS, NiS. Treat with 1 N HCl.
Solution: Zn^{++} (small amount of Co^{++}, Ni^{++}). Add NaOH, Na_2O_2 Add $(NH_4)_2S$. White precipitate: ZnS.
Precipitate: CoS, NiS. Add HCl, $KClO_3$. Evaporate, add HAc, KNO_2.
Precipitate: $K_3Co(NO_2)_6$.
Solution: Ni^{++}. Test with dimethylglyoxime for Ni^{++}.</td><td>Precipitate: Al-$(OH)_3$. Dissolve in HNO_3. Add $Co(NO_3)_2$, evaporate. Ignite. Blue residue: $Co(AlO_2)_2$.</td><td>Filtrate: $Zn(NH_3)_4^{++}$, $CrO_4^=$. Add Na_2CO_3, boil.
Precipitate: Zn-$(OH)_2$. Dissolve in HCl. Add NH_4OH, $(NH_4)_2S$. Precipitate: ZnS.
Filtrate: $CrO_4^=$. Add HAc and $PbAc_2$. Precipitate: $PbCrO_4$.</td></tr>
</table>

F. P. TREADWELL AND W. T. HALL, "Analytical Chemistry: Qualitative Analysis," J. Wiley and Sons, Inc., New York 1937:

. . . Noyes' procedure is good and I have never seen another that was based on more careful work. I have been astonished to see so few objections raised to it. . .

W. T. HALL

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

MnS, FeS, CoS, NiS, ZnS, $Al(OH)_3$, $Cr(OH)_3$. Dissolve in HCl, $KClO_3$, evaporate, treat with NaOH, Na_2O_2.

Precipitate: $Fe(OH)_3$, H_2MnO_3, $Co(OH)_3$, $Ni(OH)_2$, $Zn(OH)_2$. Dissolve in HNO_3, H_2O_2. Evaporate, boil with HNO_3, $KClO_3$.

Precipitate: MnO_2. Dissolve in HNO_3, H_2O_2. Add NaBiO$_3$. *Purple solution:* $KMnO_4$.

Solution: Fe^{++}, Co^{++}, Ni^{++}, Zn^{++}. Add NH_4OH. Filter.

Precipitate: $Fe(OH)_3$. Confirm as $Fe_4[(Fe(CN)_6]_3$.

Solution: $Co(NH_3)_6^{++}$, $Ni(NH_3)_6^{++}$, $Zn(NH_3)_6^{++}$. Saturate with H_2S, treat precipitate with 1 *N* HCl.

Residue: CoS, NiS. Dissolve in HCl, $KClO_3$. Evaporate, add HAc, KNO_2. Filter.

Precipitate: $K_3Co(NO_2)_6$.

Solution: Ni^{++}. Confirm with dimethylglyoxime.

Solution: Zn^{++}. Add NaOH, Na_2O_2. Filter, acidify with HAc, add H_2S.

Precipitate: ZnS. Confirm by Rinmann's green test.

Solution: AlO_2^-, CrO_4^{--}, $HZnO_2^-$. Acidify with HCl. Add NH_4OH.

Precipitate: $Al(OH)_3$. Dissolve in HCl and test with aluminon for Al^{+++}.

Solution: $Zn(NH_3)_4^{++}$, $CrO_4^=$. Boil with Na_2CO_3.

Precipitate: $Zn(OH)_2CO_3$. Dissolve in HCl, add NH_3, HAc, H_2S. *Precipitate:* ZnS.

Solution: $CrO_4^=$. Add HAc, $PbAc_2$. *Precipitate:* $PbCrO_4$.

J. H. REEDY, "Elementary Qualitative Analysis," 3rd Ed., McGraw-Hill Book Company, New York, 1941:

. . . $Cr(OH)_3$ is the real mischief maker. This substance carries down in its precipitation Zn^{++}, and particularly the ions of the alkaline earths and magnesium. This may be a matter of simple coprecipitation, but most authorities prefer to think that insoluble chromites are formed. This means that when Cr^{+++} is present in quantity, Zn^{++}, Ba^{++}, etc., may be wholly removed from the solution. This would cause not only failure to detect these ions in their proper places in subsequent groups, but their presence in the Al^{+++}, Cr^{+++}, Fe^{+++} group might lead to complications.

Another objection to the separation of tri- and divalent ions by selective precipitation of their hydroxides with OH^- is that iron must be completely in the form of Fe^{+++} to be thrown down. Students frequently have trouble in the complete oxidation of Fe.

The favorite procedure at this time involves the oxidation of Cr^{+++} to $CrO_4^=$ in alkaline medium, and then the separation of the combined groups on the basis of their amphoterism. That is, Al^{+++}, $CrO_4^=$, and Zn^{++} would remain in solution as AlO_2^-, $CrO_4^=$, and $HZnO_2^-$, while the rest of the ions of the combined group would be precipitated as hydroxides (or hydrated oxides). In my opinion the latter method is preferable to precipitation of hydroxides from graduated concentrations of OH^- ions, especially when chromium is present. . .

J. H. REEDY

UNIVERSITY OF ILLINOIS

$Al(OH)_3$, $Cr(OH)_3$, ZnS, MnS, FeS, NiS, CoS. Dissolve in HCl, HNO_3, boiling. Filter off S, add NaOH, Na_2O_2 and Na_2CO_3.

Filtrate: $NaAlO_2$, Na_2CrO_4, Na_2ZnO_2. Add dil. HCl, excess of NH_4OH.

Precipitate: $Al(OH)_3$, H_2SiO_3. Dissolve in hot HCl, add aluminon, neutralize with NH_4OH, heat to boiling: Al-lake.

Solution: Na_2CrO_4, $Zn(NH_3)_4^{++}$. Boil, divide. Test smaller portion with H_2SO_4, ether, H_2O_2 for Cr^{+++}.

To second portion add $BaAc_2$.

Precipitate: $BaCrO_4$.

Solution: Saturate filtrate with H_2S. *White precipitate:* ZnS.

Precipitate: MnO_2, $Fe(OH)_3$, $Ni(OH)_2$, $Co(OH)_3$. Add conc. HNO_3, boil. Add $NaNO_2$, solid $KClO_3$. Filter on asbestos.

Residue: MnO_2. Add PbO_2, dil. HNO_3, boil. *Solution:* purple $HMnO_4$.

Filtrate: Fe^{+++}, Ni^{++}, Co^{++}. Add NH_4OH in excess.

Precipitate: $Fe(OH)_3$. Dissolve in HCl. Confirm with SCN^- and also with $K_4Fe(CN)_6$.

Filtrate: $Ni(NH_3)_4^{++}$, $Co(NH_3)_6^{++}$. Divide.

Acidify with HAc. Add dimethylglyoxime. *Red precipitate:* Ni-dimethylglyoxime.

Acidify with conc. HCl. Add NH_4SCN, amyl alcohol ether, shake. Blue-green layer indicates Co^{++}.

D. ZnS precipitated from weakly acid solution: This group of methods makes use of the fact the Zn^{++} is the only ion of Group III which can be precipitated as sulfide from slightly acidic solution (see also Barber and Taylor, part F, of this survey). Meldrum and Daggett use monochloracetic acid-ammonium monochloracetate as buffer for the precipitation of zinc sulfide in the presence of any or all the other ions of Group III.

Hogness and Johnson (*35*) dissolve the sulfides or hydroxides of Al^{+++}, Cr^{+++}, Fe^{+++}, and Mn^{++} by the use of the weakest acid ($NaHSO_4$-Na_2SO_4), leaving the undissolved sulfides of Co^{++}, Ni^{++}, and Zn^{++} as residue. Later Zn^{++} is precipitated as sulfide from the weakest acid solution, buffered by $NaHSO_4$-Na_2SO_4.

W. B. MELDRUM AND A. F. DAGGETT:

. . . I have now the results, obtained by students at Haverford College and also here at the University of New Hampshire, using our revised Group III procedure; I am taking the liberty of enclosing a copy of it for your use.

The results obtained using the new procedure appear to be very satisfactory. The difficulty experienced with our original procedure, of the interference of nickel and cobalt with the confirmatory test for zinc, has now been eliminated.

This revised procedure will appear in our new book to be published during the coming year (1946). . .

A. F. DAGGETT

UNIVERSITY OF NEW HAMPSHIRE

Add NH_4Cl, 15 *M* NH_4OH in excess. Heat. Saturate with H_2S. Centrifuge. Add 15 *M* NH_4OH and saturate with H_2S again. Wash. Add 12 *M* HCl, 16 *M* HNO_3. Heat. Add 15 *M* NH_4OH, 4 *M* monochloracetic acid. Heat. Add H_2S.

Precipitate: White or gray precipitate, zinc. Confirm by adding HCl. Warm. If precipitate dissolves, zinc confirmed.

Solution: Co^{++}, Ni^{++}, Al^{+++}, Cr^{+++}, Mn^{++}, Fe^{++}. Boil to remove H_2S. Add Br_2-water, 15 *M* NH_4OH, 3 *M* $(NH_4)_2CO_3$.

Precipitate: Mn^{++}, Fe^{+++}, Al^{+++}, Cr^{+++}. Add 15 *M* NH_4OH, 12 *M* HCl, NaOH, 3% H_2O_2. Heat.

Precipitate: Mn^{++}, Fe^{+++}. Add HNO_3 Heat.

Precipitate: indicates Mn^{++}. Add HNO_3, 3% H_2O_2, HNO_3, $NaBiO_3$, MnO_4^-.

Solution: Fe^{+++}. Add NH_4OH, HCl, $K_4Fe(CN)_6$. *Precipitate:* $Fe_4[Fe(CN)_6]_3$.

Solution: Cr^{+++}, Al^{+++}. Boil. Add HNO_3, 15 *M* NH_4OH.

Precipitate: $Al(OH)_3$. Dissolve in HCl. Add NH_4Ac, aluminon, NH_4OH, $(NH_4)_2CO_3$. Heat. *Precipitate:* Al-lake.

Solution: Cr^{+++}. Add CH_3COOH, $PbAc_2$. *Precipitate:* $PbCrO_4$.

Solution: Co^{++}, Ni^{++}. Add CH_3COOH. Divide.

Add dimethyl glyoxime and NH_4OH. *Precipitate:* Ni-dimethyl glyoxime.

Add α-nitroso-β naphthol solution. *Precipitate:* Co^{++}.

Further test: Add KNO_2. Warm. *Precipitate:* $K_3Co(NO_2)_6$.

T. R. HOGNESS AND W. C. JOHNSON, "Qualitative Analysis and Chemical Equilibrium," Henry Holt and Company, New York, **1940:**

. . . It is of advantage to identify the zinc first, since the usual difficulty in the determination of zinc, *i.e.*, coprecipitation with chromium and manganese, is avoided. . .

T. R. HOGNESS

UNIVERSITY OF CHICAGO

. . . Dr. Hogness and I have never been particularly impressed by the need for a perfect analytical procedure of the type commonly used in the teaching of qualitative analysis. There are many reasons for making such a statement. One is that when a student gets into industrial work or into research of any type, he will never use these procedures for analytical purposes excepting in a general way as they apply to the separation of groups of elements. The new procedures—such as spectrographic, colorimetric, spectrophotometric, and highly specialized precipitation procedures—which have been developed during the past twenty years, are so much more rapid, accurate, and practical. . . . The important function of teaching qualitative analysis as we do is to teach the student the chemistry of the ions and to give him a working basis for the application of the Law of Mass Action. The analytical procedure is merely an excellent medium for accomplishing these two aims. A third aim is the development of techniques, especially those employed in the semimicro scale, in handling solutions and separating the different components from each other. While it would be nice to have a perfect scheme, it appears to us that this is of secondary importance. As a result I would be more inclined to place in a qualitative analysis procedure as many elements as possible consistent with the teaching of the chemistry of different types of ions and with ease of separation of the ions. . .

WARREN C. JOHNSON

UNIVERSITY OF CHICAGO

<table>
<tr><td colspan="5">$Al(OH)_3$, $Cr(OH)_3$, FeS, MnS, ZnS, CoS, NiS.
Add saturated Na_2SO_4 and 2 M $NaHSO_4$.</td></tr>
<tr><td>Residue: ZnS, CoS, NiS. Dissolve in HCl and HNO_3, evaporate, add Na_2SO_4 and $NaHSO_4$. Add H_2S.
Precipitate: ZnS.</td><td colspan="4">Solution: Al^{+++}, Cr^{+++}, Fe^{++}, Mn^{++}. Add H_2SO_4, boil; add Br_2-water, boil, add NH_4OH.</td></tr>
<tr><td></td><td>Solution: Co^{++}, Ni^{++}. Boil, add Br_2-water. Divide.</td><td colspan="3">Precipitate: $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$, $Mn(OH)_3$. Dissolve in HCl, treat with NaOH. Add 3% H_2O_2.</td></tr>
<tr><td></td><td>Add KNO_2. Precipitate: $K_3[Co(NO_2)_6]$</td><td>Add NH_4OH and dimethylglyoxime.
Precipitate: Ni-dimethylglyoxime.</td><td>Residue: $Fe(OH)_3$, MnO_2. Add HCl, KCNS. Red color shows Fe^{++}.</td><td>Solution: AlO_2^-, $CrO_4^=$. Add HCl, NH_4OH.
Precipitate: $Al(OH)_3$. Add HCl, aluminon, NH_4OH.
Precipitate: Al-lake.
Solution: $CrO_4^=$. Add HAc and $PbAc_2$.
Precipitate: $PbCrO_4$.</td><td>Solution: Mn^{++}. Add HNO_3, $NaBiO_3$.
Purple color: MnO_4^-.</td></tr>
</table>

E. MnO_2 separated first: Advantage can be taken of the fact that MnO_2 is only slightly soluble, and an early attempt to use this fact by oxidizing Mn^{++} in NaAc solution by chlorine gas was made by Schiel and is called "ingenious" by Muspratt [(*53*) Vol. 2, p. 544]. However, the application of chlorine gas is cumbersome and impractical, so Curtman (*34*) has proposed oxidation by $KClO_3$ to obtain MnO_2 as the first step in his text. In the next step $Fe(OH)_3$ and $Al(OH)_3$ are precipitated while $CrO_4^=$ and the ammonia complexes of Co^{++}, Ni^{++}, and Zn^{++} remain in solution. $CrO_4^=$ can then be identified as $BaCrO_4$ while the separation of the remaining ions, Ni^{++}, Co^{++}, and Zn^{++}, is carried out simply by precipitation of $Co(OH)_3$ and $Ni(OH)_2$ with strong alkali which keeps $ZnO_2^=$ in solution.

L. J. CURTMAN, "Semimicro Qualitative Analysis," The Macmillan Company, New York, **1942:**

. . . It is well known by laboratory workers in the analytical field that in the analysis of the Group III cations, manganese is a troublesome element. It occurred to me that if I could remove it at the outset of the analysis by precipitation with $KClO_3$ in HNO_3 solution, I would be able to simplify the analysis. Experiment showed that this could be done. This procedure has the further advantage of simultaneously oxidizing Cr^{+++} to $CrO_4^=$ at the beginning of the analysis, thus supplying an additional step in the simplification of the procedure. . .

. . . The separation of Ni^{++} and Co^{++} from Zn^{++} by means of NaOH and Na_2O_2, if properly carried out, is very satisfactory.

Finally, the Zn^{++} is precipitated by H_2S in the NaOH filtrate. A white precipitate must be Zn^{++}, since any undecomposed peroxide left in the solution does *not* oxidize the H_2S to S when the solution is alkaline, a fact confirmed by many experiments. . .

L. J. CURTMAN

THE COLLEGE OF THE CITY OF NEW YORK

<table>
<tr><td colspan="5">$Al(OH)_3$, $Cr(OH)_3$, FeS, NiS, CoS, MnS, ZnS. Dissolve in HCl-HNO_3, evaporate.
Add $KClO_3$, heat, centrifuge.</td></tr>
<tr><td>Residue: MnO_2. Confirm with Na_2CO_3, $KClO_3$ bead, or convert to MnO_4^-.</td><td colspan="4">Solution: Al^{+++}, $Cr_2O_7^=$, Fe^{+++}, Ni^{++}, Co^{++}, Zn^{++}. Remove excess HNO_3 by evaporation. Add NH_4NO_3 and NH_3. Centrifuge.</td></tr>
<tr><td></td><td colspan="4">Residue: $Fe(OH)_3$, $Al(OH)_3$. Add excess NaOH. Centrifuge.</td></tr>
<tr><td></td><td>Residue: $Fe(OH)_3$.</td><td>Solution: $Al(OH)_4^-$.</td><td colspan="2">Solution: $CrO_4^=$, $Ni(NH_3)_6^{++}$, $Co(NH_3)_6^{++}$, $Zn(NH_3)_4^{++}$. Add $BaCl_2$.
Residue: $BaCrO_4$.</td></tr>
<tr><td></td><td></td><td></td><td colspan="2">Solution: $Ni(NH_3)_6^{++}$, $Co(NH_3)_6^{++}$, $Zn(NH_3)_6^{++}$. Add H_2S and discard solution. Dissolve NiS, CoS, and ZnS in HNO_3. Add NaOH, Na_2O_2. Centrifuge.</td></tr>
<tr><td></td><td></td><td></td><td colspan="2">Residue: $Ni(OH)_3$, $Co(OH)_3$. Dissolve in HCl, neutralize with NaOH, acidify with HAc. Divide.
Test for Ni^{++}. | Test for Co^{++}.</td></tr>
<tr><td></td><td></td><td></td><td colspan="2">Solution: $Zn(OH)_4^=$. Treat with H_2S.
Precipitate: ZnS.</td></tr>
</table>

F. Precipitation with NH_4OH in H_2S-free solution followed by precipitation of filtrate with $(NH_4)_2S$: In this way Group III is divided into two independent groups: the iron group and the nickel group. Six analytical groups result in this way—Group I: Ag^+, Hg_2^{++}, Pb^{++}; Group II: the eight usual ions; Group III: Al^{+++}, Cr^{+++}, Fe^{+++}; Group IV: Co^{++}, Ni^{++}, Zn^{++}, Mn^{++} (or Mn^{++} may be placed in Group III); Group V: Ca^{++}, Ba^{++}, Sr^{++}; Group VI: alkali metals. This method is used in the textbooks of Kelsey and Dietrich (*36*) and of Barber and Taylor (*37*). According to both methods, the iron has to be oxidized to the trivalent form. Whereas Kelsey and Dietrich use concentrated HNO_3 as an oxidizing agent, Barber and Taylor use Br_2-water in ammoniacal solution. This brings about a minor variation between the two methods; only the iron is oxidized by HNO_3 while manganese is left in the divalent (soluble) form. Kelsey

and Dietrich treat Fe^{+++}, Al^{+++}, and Cr^{+++} as one group; however, since manganese is oxidized by Br_2-water to the trivalent form, it is precipitated together with Fe^{+++}, Al^{+++}, and Cr^{+++} ions in the Barber-Taylor system. The further analysis of the iron group makes use of the formation of AlO_2^- and $CrO_4^=$, which stay in solution while $Fe(OH)_3$ [in Barber and Taylor's book, $Fe(OH)_3$ and $Mn(OH)_3$] is precipitated. The two texts differ also regarding the Ni^{++} group. Kelsey and Dietrich convert Co^{++}, Ni^{++}, Mn^{++}, and Zn^{++} into sulfides and separate the insoluble CoS and NiS (2 *M* HCl) from Mn^{++} and Zn^{++}; Barber and Taylor precipitate ZnS in HAc solution the *p*H of which does not allow the precipitation of Ni^{++} or Co^{++}.

E. B. KELSEY AND H. G. DIETRICH, "Fundamentals of Semimicro Qualitative Analysis," The Macmillan Company, New York, **1940:**

. . . There are two closely associated reasons why the authors of "Semimicro Qualitative Analysis" chose to separate the cations of Group III as we do.

The text is designed for one term courses in analysis. The chief emphasis is on principles of analysis rather than on a detailed study of analytical reactions. These principles seem to be brought out better by the use of two separate groups than by combining the ions into a single group. If the seven cations involved are considered in a group, we feel that the student tends to become confused with details of procedure and learns less of the actual principles involved. Experience bears out these views. . .

E. B. KELSEY

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Fe^{++}, Al^{+++}, Cr^{+++}, Co^{++}, Ni^{++}, Mn^{++}, Zn^{++}.
Add conc. HNO_3, heat, dilute, add NH_4Cl. Make alkaline with NH_4OH, filter, wash.

Precipitate: (Iron Group) $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$. Add NaOH, H_2O_2, stir, heat.			*Solution:* (Nickel Group) Co^{++}, Ni^{++}, Mn^{++}, Zn^{++}. Pass H_2S into solution, filter. Treat precipitate with *M* HCl.			
Residue: $Fe(OH)_3$. Confirm presence of Fe^{+++}.	*Solution:* AlO_2^-, $CrO_4^=$. Add solid NH_4Cl.		*Residue:* CoS, NiS. Divide:		*Solution:* Mn^{++}, Zn^{++}. Evaporate, make alkaline with NaOH, filter.	
	Precipitate: $Al(OH)_3$. Dissolve in HCl, add NH_4Ac, aluminon, NH_4OH. *Precipitate:* Al-lake.	*Solution:* $CrO_4^=$. Acidify with HAc, add $PbAc_2$. *Precipitate:* $PbCrO_4$.	*Residue:* Test with Borax bead for Co^{++}.	*Residue:* Dissolve in aqua regia. Evaporate. Dissolve in H_2O. Add NH_3, test with dimethylglyoxime for Ni^{++}.	*Precipitate:* $Mn(OH)_2$. Dissolve in HNO_3, add $NaBiO_3$. *Purple color:* MnO_4^-.	*Solution:* $ZnO_2^=$. Acidify with HAc, add H_2S. *Precipitate:* ZnS.

H. H. BARKER AND T. I. TAYLOR, "Semimicro Qualitative Analysis," Harper Brothers, New York, **1942:**

. . . The Group III may be separated into one group as hydroxides, and then into another group as sulfides. The latter method is followed in the Barber-Taylor text, for the following reasons:

In semimicro qualitative analysis, the volume is small, consequently the filtrate from Group II may easily and quickly have the hydrogen sulfide removed by boiling. The filtrate is now an acid solution without hydrogen sulfide. By the addition of ammonium hydroxide and bromine water the hydroxides of aluminum and chromium (Cr^{+++}) will be precipitated, and the ferrous ions will be oxidized to ferric ions, and the latter will be precipitated as ferric hydroxide; the Mn^{++} will be oxidized to Mn^{+++} and will be precipitated as $Mn(OH)_3$ or maybe $MnO(OH)_2$, while the zinc, cobalt, and nickel ions will form ammonia complexes and remain in solution. . .

H. H. BARBER

UNIVERSITY OF MINNESOTA

Al^{+++}, Cr^{+++}, Fe^{++}, Mn^{++}, Co^{++}, Ni^{++}, Zn^{++}.
Add NH_4Cl, NH_4OH, heat, add Br_2-water.

Precipitate: (Iron Group) $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$, $Mn(OH)_3$. Add NaOH, H_2O_2, boil.				*Solution:* (Nickel Group) Co^{++}, Ni^{++}, Zn^{++}. Boil, add HAc saturate with H_2S.			
Solution: AlO_2^-, $CrO_4^=$, $ZnO_2^=$. Divide. If solution yellow, test for Zn^{++}.		*Residue:* $Fe(OH)_3$, $Mn(OH)_3$. Add HNO_3 and hydroxylamine hydrochloride (or H_2O_2). Divide.		*Precipitate:* ZnS. Confirm if necessary. Dissolve in HCl. Boil, add NH_4Ac and 8-hydroxyquinoline.	*Filtrate:* Ni^{++}, Co^{++}. Add NH_4OH $(NH_4)_2S$.		
Acidify with HAc. Add aluminon and $(NH_4)_2CO_3$. *Precipitate:* Al-lake.	Acidify with HAc. Add $PbAc_2$. *Precipitate:* $PbCrO_4$.	Add $K_4Fe(CN)_6$ or NH_4SCN to determine presence of Fe^{+++}.	Add $NaBiO_3$. *Purple color:* MnO_4^-.		*Precipitate:* NiS, CoS. Add NaClO, HCl. Boil. Divide: Test for Ni with dimethylglyoxime, and for Co with nitroso-R-salt.	*Solution:* Later groups.	

LITERATURE CITED

I. *General References:*

A. Dry Methods:

(1) TREADWELL, F. P., "Analytische Chemie," Vol. I, Franz Deuticke, Leipzig, **1927**, p. 431.

(2) LUTZ, O., *Z. anal. Chem.*, **47**, 1 (1908).

B. Optical methods:

(3) KAYSER, H., "Handbuch der Spectroscopie," S. Hirzel, Leipzig, **1901–12.**

(4) BRODE, W. R., "Chemical Spectroscopy," John Wiley and Sons, Inc., New York, **1939.**

(5) GERLACH, W., ET AL., "Die chemische Emissions-Spektralanalyse," Voss, **1929, 1933, 1936.**

(6) SCHEIBE, G., "Spektroskopische und radiometrische Analyse," Akad. Verlagsgesellschaft, Leipzig, **1933.**

(7) SMITH, D. M., "Metallurgical Analysis by the Spectrograph," Metals Research Association (Brit.) Monograph 2, 1933.

C. Wet methods:

1. Spot tests:

(8) FEIGL, F., "Spot Tests," Translated by J. W. Matthews, Nordemann Publishing Company, New York, **1937.**

(9) FEIGL, F., AND H. A. SUTER, *Chemist-Analyst*, **32**, 4–6 (1943).

(10) FEIGL, F., P. KRUMHOLZ, AND H. HAMBURG, *Z. anal. Chem.*, **90**, 199–202 (1932).

(11) FEIGL, F., AND H. J. KAPULITAS, *Z. anal. Chem.*, **82**, 417–25 (1930).

(12) TANANAEV, N. A., *Z. anorg. allgem. Chem.*, **140**, 320–34 (1924).

2. Polarographic technique:

(13) MUELLER, O. H., "Polarographic Method of Analysis," J. CHEM. EDUC., Easton, Pennsylvania, **1945.**

3. Precipitation (without H_2S):

(14) CHAO, T. P., AND S. C. HWANG, *J. Chinese Chem. Soc.*, **8**, 21–31 (1941).

(15) ZELADA, F., *Anales asoc. quim. argentina*, **30**, 29 (1942).

(16) KHOROSHKIN, M. N., *Acta Univ. Voronegiensis*, **10**, 95–102 (1939).

(17) SHCHIGOL, M. B., AND M. DUBINSKII, *Ann. chim. anal. chim. appl.*, **18**, 257–62 (1936).
(18) LEWIN, A. B., *Z. anal. Chem.*, **105**, 328–31 (1936).
(19) GERSTENZANG, E. M., J. CHEM. EDUC., **11**, 369–73 (1934).
(20) KOMAROVSKII, A. S., AND V. I. GOREMUIKIN, *J. Applied Chem.* **4**, 877–80 (1931).
(21) PAMFIL, G. P., *Mon. sci.*, **24**, 641–43 (1910).
(22) TRAPP, H., *Z. anal. Chem.*, **51**, 475 (1912).
(23) PURGOTTI, A., *Gazz. chim. ital.*, **42**, II, 58–67 (1911).
(24) ALMKVIST, G., *Z. anorg. allgem. Chem.*, **103**, 221–39 (1918).
(25) DOBBINS, J. T., AND E. S. GILREATH, J. CHEM. EDUC., **22**, 119 (1945).

4. Precipitation (with H_2S):
(26) HEISIG, G. B., "Semi-micro Qualitative Analysis," W. B. Saunders Company, New York, **1943**.
(27) MELDRUM, W. B., E. W. FLOSDORF, AND A. F. DAGGETT, "Semi-micro Qualitative Analysis," American Book Company, New York, **1939**.
(28) TREADWELL, F. P., AND W. T. HALL, "Analytical Chemistry: Qualitative Analysis," John Wiley and Sons, Inc., New York, **1903, 1937**.
(29) VOSBURGH, W. C., "Introductory Qualitative Analysis," Macmillan Company, New York, **1938**.
(30) SWIFT, E. H., "A System of Chemical Analysis," Prentice-Hall, Inc., New York, **1939**.
(31) NOYES, A. A., AND E. H. SWIFT, "Qualitative Chemical Analysis," Macmillan Company, New York, **1942**.
(32) NOYES, A. A., "Qualitative Chemical Analysis," Macmillan Company, New York, **1942**.
(33) REEDY, J. H., "Elementary Qualitative Analysis," 3rd Ed., McGraw-Hill Book Company, New York, **1941**.
(34) CURTMAN, L. J., "Semimicro Qualitative Analysis," Macmillan Company, New York, **1942**.
(35) HOGNESS, T. R., AND W. C. JOHNSON, "Qualitative Analysis and Chemical Equilibrium," Henry Holt and Company, New York, **1940**.
(36) KELSEY, E. B., AND H. G. DIETRICH, "Fundamentals of Semimicro Qualitative Analysis," Macmillan Company, New York, **1940**.
(37) BARBER, H. H., AND T. I. TAYLOR, "Semimicro Qualitative Analysis," Harper and Brothers, New York, **1942**.

II. Special References to Group III:

A. Organic Reagents:
(38) ROSSI, L., AND R. G. CORNATO, *Rev. assoc. bioquim., argentina*, **7**, 11–20 (1941).
(39) KOENIG, E. W., *Chemist-Analyst*, **30**, 15 (1941).
(40) ROSSI, L., AND A. TRONCOSO, *Rev. assoc. bioquim. argentina*, **4**, 11–24 (1939).
(41) ROSSI, L., C. A. LANARO, AND I. LUSIN, *ibid.*, **3**, 5–6 (1938).
(42) LEHRMAN, L., H. WEISBERG, AND E. A. KABAT, *J. Am. Chem. Soc.*, **56**, 1836–38 (1934).
(43) BELOUSOU, A. M., AND A. G. BELOUSOVA, *J. Applied Chem.*, **7**, 837–8 (1934).
(44) FUNK, H., AND M. DITT, *Z. anal. Chem.*, **91**, 332–40 (1933).
(45) SHEINKMAN, A., *ibid.*, **83**, 176–88 (1931).
(46) YU, T. L., *Science (China)*, **14**, 810–20 (1930).
(47) GROSSMANN, H., B. SCHUCK, AND W. HEILBORN, *Bull. soc. ind. Rouen*, **38**, 116–127 (1910).
(48) SANCHEZ, J. A., *Bull. soc. chim.*, **9**, 880–1.
(49) WENGER, P., R. DUCKERT, AND D. RIETH, *Helv. Chim. Acta*, **25**, 406–15 (1942).
(50) BRYANT, W. M. D., J. MITCHELL, JR., D. M. SMITH, AND E. C. ASHBY, *J. Am. Chem. Soc.*, **63**, 2924–7 (1941).
(51) BLICK, D. J., *Rept. New Engl. Assoc. Chem. Teachers*, **43**, No. 1, 13–19 (1941).
(52) YOE, J. H., AND L. A. SARVER, "Organic Analytical Reagents," John Wiley and Sons, Inc., New York, **1941**, pp. 263–326.

B. Nickel Ion:
(53) MUSPRATT, J. S., Vol. II, Glasgow, **1860**, p. 591. Quotes Liebig on separation of cobalt from nickel.
(54) THIEL AND GESSNER, *Z. anorg. Chem.*, **86**, 1 (1914).
(55) TSCHUGAEFF, L., *Ber.*, **38**, 2520 (1905).
(56) BRUNCK, O., *Zeit. angew. Chem.*, **20**, 1844 (1907); *ibid.*, **27**, 315 (1914).
(57) FEIGL, F., *Ber.*, **57B**, 759 (1924).
(58) HELLER, K., AND P. KRUMHOLZ, *Mikrochemie*, **7**, 213 (1929).

C. Cobalt Ion:
(59) VOGEL, H. W., *Ber.*, **12**, 2314 (1879).
(60) TREADWELL, *Z. anorg. allgem. Chem.*, **26**, 105 (1901).
(61) MORRELL, T. T., *Z. anal. Chem.*, **16**, 251 (1877).
(62) REEDY, J. H., "Theoretical Qualitative Analysis," McGraw-Hill Book Company, Inc., New York, **1938**, p. 262.
(63) FEIGL, F., AND R. STERN, *Z. anal. Chem.*, **60**, 31 (1921).
(64) ATACK, F. W., *J. Soc. Chem. Ind.*, **34**, 641 (1915).
(65) ILINSKY-KNORRE, *Ber.*, **18**, 699 (1885).

D. Aluminum Ion:
(66) HAMMETT, L. P., AND C. T. SOTTERY, *J. Amer. Chem. Soc.*, **47**, 142 (1925).
(67) REEDY, J. H., "Theoretical Qualitative Analysis," McGraw-Hill Book Company, Inc., New York, **1938**, p. 245.

E. Zinc Ion:
(68) AGOSTINI, P., *Ann. chim. applicata*, **19**, 164 (1929).
(69) SENSI, C., AND R. TESTORI, *Ann. chim. applicata*, **19**, 383 (1929).
(70) REEDY, J. H., "Theoretical Qualitative Analysis," McGraw-Hill Book Company, Inc., New York, **1938**, pp. 252, 279.

F. Manganese Ion:
(71) FEIGL, F., AND R. STERN, *Z. anal. Chem.*, **60**, 24 (1921).
(72) REEDY, J. H., "Theoretical Qualitative Analysis," McGraw-Hill Book Company, Inc., New York, **1938**, p. 253.
(73) CRUM, *Ann. Chim.*, **198**, 362 (1879).

G. Chromate Ion:
(74) KARLSLAKE, W. J., *J. Amer. Chem. Soc.*, **31**, 250 (1909).
(75) RIESENFELD, E., *Ber.*, **47B**, 548, 553 (1914).
(76) FRESENIUS, W., AND F. RUPPERT, *Z. anal. Chem.*, **30**, 677 (1891).
(77) WEINLAND, R., AND E. GIESSMANN, *Ber.*, **42**, 3881 (1909); *Z. anorg. Chem.*, **66**, 157 (1910).
(78) CAZENEUVE, P., *Chem. Zentr.*, **2**, 709 (1901).

H. Ferric Ion:
(79) ROSENHEIM, A., *Z. anorg. Chem.*, **27**, 298 (1901).
(80) HELLER, K., AND P. KRUMHOLZ, *Mikrochemie*, **7**, 213 (1929).
(81) SCHLESINGER, H. J., AND H. B. VAN VALKENBURGH, *J. Amer. Chem. Soc.*, **53**, 1212 (1931).
(82) ARDAGH, E. G. R., AND G. R. BONGARD, *Ind. Eng. Chem.*, **16**, 297–99 (1924).

"....Modern university education in science and technology lays altogether too much emphasis on the working of things, and gives insufficient attention to human relationships and the working of the mind. Graduates are of much greater value to industry when, in addition to an equipment of mathematical and scientific data, they possess some knowledge of humanity with its intricate and sometimes contradictory relationships...."—Dr. Percy Dunsheath, director and chief engineer, Henley's Telegraph Works, Ltd.

FIGURE 1. OLEFIN-POLYSULFONE RESINS. THYON MOLDING POWDER PREPARED FROM AN OLEFIN MIXTURE CONSISTING OF 50 PER CENT PROPYLENE, 33 PER CENT BUTENE-2, AND 17 PER CENT BUTENE-1—A LUMP OF THE CRUDE RESIN; A MACHINE-THREADED STUD, POKER CHIPS, AND DISC.

(Courtesy of F. E. Frey of the Phillips Petroleum Company)

Reactions of Sulfur Dioxide with Unsaturated Hydrocarbons[1]

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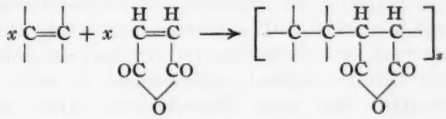
IN THE course of other work on oils and resins we became interested a few years ago in some organic compounds known as sulfones. Sulfones are compounds which contain the divalent sulfur dioxide group attached to two carbon atoms. The simplest member of this very large class is dimethyl sulfone, $CH_3—SO_2—CH_3$. Other examples of interest include the hypnotic sulfonal $(CH_3)_2C(SO_2C_2H_5)_2$; di-(*p*-chlorophenyl) sulfone $(p\text{-}ClC_6H_4)_2SO_2$, an insecticide developed by J. R. Geigy Company prior to DDT; and di-(*p*-aminophenyl) sulfone, $(p\text{-}NH_2C_6H_4)_2SO_2$, a drug with properties somewhat resembling the sulfa compounds.

The synthesis of sulfones can be carried out in several different ways, but the particular route to be discussed here is the direct reaction of sulfur dioxide with unsaturated hydrocarbons. Such reactions were first studied about 50 years ago, but most of the work has been done in the past 15 years. In this country Frey and Snow of the Phillips Petroleum Company and Marvel at the University of Illinois have been leaders in the field.

POLYSULFONES

The first reaction to be considered is one of polymerization. Sulfur dioxide adds to carbon-carbon unsaturation to form long linear molecules known as polysulfones in which the hydrocarbon radical and sulfone group alternate:

Both the addition to a double bond and the increase in the valence of sulfur from four to six are well-known changes,[2] but the *combination* of these two changes as a polymerization process is the noteworthy aspect of this reaction. In a sense, this reaction might be termed a copolymerization, although the sulfur dioxide is not polymerizable itself, and is thus comparable to the copolymerization of certain olefins and maleic anhydride, maleic anhydride being the nonpolymerizable component:



Although not all unsaturated hydrocarbons will form polysulfones, many olefins, diolefins, and acetylenes do, as well as certain of their derivatives such as alcohols, aldehydes, and acids. Mixtures of these compounds such as two olefins, or an olefin with an

[1] Presented before the Technical Society of the Sherwin-Williams Company, Chicago, Illinois, October 23, 1945. Based on the M.A. thesis of Alan Ardis, Western Reserve University, 1944.

[2] This view of the valence change of sulfur is strictly an elementary one; for example, tetravalent sulfur in sulfur dioxide, hexavalent sulfur in sulfur trioxide. For a more extended discussion of the nature of the bonds in sulfones, see (*6*), p. 658.

unsaturated compound, such as pentene-1 with undecylenic acid, also react with sulfur dioxide, forming complex polysulfones.

(*a*) *Preparation of Polysulfones.* Polysulfone reactions are carried out in the liquid phase usually with excess sulfur dioxide, although theoretically only one mol is required per mol of olefin. The excess serves as solvent, keeping the polysulfone in solution until high molecular weights are reached, and also off-setting the loss of sulfur dioxide due to absorption by the product. Moderate temperatures of 0–30° are usually employed. In order for polymerization to occur, the reaction mixture must either be exposed to light or a suitable catalyst must be present. In the absence of light or catalyst, olefin-sulfur dioxide mixtures have stood for as long as one year without reacting. Apparently the light or catalyst does more than simply accelerate a slow reaction. One of the agents is necessary to *initiate* the reaction.

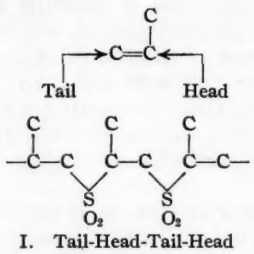
For the photochemical reaction, light in the range of 3000–3800 A. U. is effective, probably because sulfur dioxide shows a strong absorption at 3100 A. U. The reaction is run more conveniently and with better control, however, if a catalyst is used instead of light. Among the classes of compounds from which catalysts may be selected are the amine oxides, metallic chlorates, metallic nitrates, ozonides, peracids, and peroxides. Catalysts frequently used are silver nitrate, peracetic acid, and ascaridole—usually introduced into the reaction mixture as an alcoholic solution. It will be noted that these catalysts are all oxygen-bearing compounds with more or less oxidizing power. Catalysts having too strong an oxidizing action, such as nitric acid, are not suitable, because some sulfur dioxide is oxidized to sulfur trioxide which leads to dark-colored resins, contaminated with polymerized hydrocarbons whose formation was catalyzed by sulfur trioxide (or sulfuric acid).

As the polysulfone reaction progresses, there is a contraction in liquid volume, an increase in viscosity, heat is liberated, and finally the polysulfone precipitates. Study of the change in reaction rate with temperature has shown that the temperature coefficient is negative and that the reaction stops rather sharply at a temperature known as the ceiling temperature. With isobutylene, for example, polysulfone formation proceeds smoothly at 0° but stops completely at 4–5°. By lowering or raising the temperature slightly the reaction can be started and stopped at will. This phenomenon has been observed for other olefins: propylene has a ceiling temperature at 87–89°; butene-1 at 63–66°; and butene-2 at 43–45°. The ceiling temperature appears to be characteristic of the olefin and independent of concentration and catalyst. Furthermore, the ceiling temperature is lowest for the olefins which most readily polymerize in the presence of acid catalysts, *i. e.*, isobutylene catalyzed by sulfuric acid polymerizes more readily than propylene, butene-1, or butene-2. There is no satisfactory explanation for this phenomenon other than the suggestion that at and above the ceiling temperature there is formed some inhibiting substance of unknown composition which is not formed or only formed in ineffectual amounts at lower temperatures.

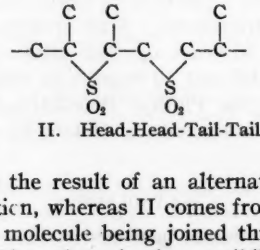
Another peculiar property of these polysulfone reactions is the retardation of polysulfone formation from sulfur dioxide and one olefin by the presence of small amounts of another olefin, although each olefin by itself is capable of polysulfone formation. For example, 10 per cent of isobutylene reduces the rate of the butene-1-sulfur dioxide reaction at room temperature to about one-tenth of its normal value. The fact that room temperature is above the ceiling temperature of isobutylene suggests that the inhibiting substance hypothesized for the ceiling temperature may be formed in this reaction mixture and may act as a negative catalyst.

(*b*). *Structure of the Polysulfones.* As a result of the work of Marvel and his students, the structure of the olefin polysulfones is well understood. In the case of symmetrical olefins, such as butene-2 and cyclohexene, the structure of the polysulfone is simply that of alternate hydrocarbon and sulfone groups. The end groups of these linear molecules are apparently derived from water. A hydrogen atom is attached to one terminal carbon atom and a hydroxyl group to the other, or in a few cases there may be a terminal sulfone group to which is attached a hydroxyl to make a terminal sulfonic acid group. The length of these chains varies with the olefin and reaction conditions, and molecular weights of 50,000 to 280,000 have been reported.

When the olefin is unsymmetrical, the possible structure of the polysulfone is more complex because of the two possible modes of addition of sulfur dioxide to the carbon-carbon double bond:



I. Tail-Head-Tail-Head



II. Head-Head-Tail-Tail

Structure I is the result of an alternating tail-head-tail-head addition, whereas II comes from like ends of the propylene molecule being joined through the sulfone group. Also, there is the possibility that both types of structure occur in a single molecule, or that some molecules form according to I, others according

to II. The details of the structure determination need not be considered here, but important evidence was obtained by study of the products formed from propylene polysulfone plus sodium hydroxide, in the light of the fact that carbon-sulfur linkages where the carbon atom is secondary are more readily cleaved than carbon-sulfur linkages where the carbon atom is primary. It should be noted that bonds formed at the head of the propylene molecule are secondary, at the tail, primary. From this study, structure II was clearly established, and this type of structure appears to be general for polysulfones derived from olefins having a terminal double bond, prepared either by a photochemical or by a peroxide-catalyzed reaction.

When an equimolar mixture of two olefins or olefin derivatives is reacted with sulfur dioxide, true copolymers are formed, *i. e.*, each molecule contains both of the reactants alternately linked to the sulfone group in the head-head-tail-tail structure. An example of this type of copolymer is the polysulfone derived from pentene-1 and undecylenic acid.

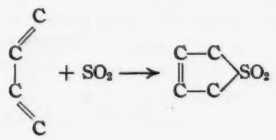
(*c*) *Properties of the Polysulfones.* Physical properties of the polysulfones vary with the olefin taken, but they are all thermoplastic, resinous substances. Low molecular weight olefins give hard, high-melting, opaque, or transparent solids, while long chain olefins yield softer, more plastic and rubbery products. Resins derived from olefins where the double bond is between carbon atoms two and three are higher melting and less soluble than resins from isomeric olefins having a terminal double bond. The polysulfones are insoluble in water, acids, most organic solvents, and usually insoluble in dilute alkalies. In combination with plasticizers, fillers, and pigments they can be molded by the usual techniques (Figure 1). When deposited from solution onto surfaces, coating films are formed.

Like most other synthetic resins, the polysulfones have certain undesirable properties. Instability, especially at temperatures above the softening temperature, which is usually over 200°, permits decomposition to sulfur dioxide, the olefin, and other compounds. Progress has been made in increasing stability by removing from the crude resin the last traces of absorbed sulfur dioxide and peroxidic compounds, the latter apparently catalyzing decomposition. These improvements along with the development of heat stabilizing agents are said to have produced satisfactory resins from the standpoint of fabrication.

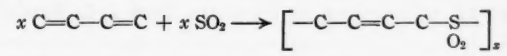
Although chemical stability to water, dilute acids, and organic solvents is good, all of the polysulfones are destroyed by concentrated alkalies through cleavage of the carbon-sulfur bonds. Despite the tendency toward instability and the sensitivity to alkali, the relatively low cost of these resins and the modifications which may come from further development should eventually bring them into large-scale use.

UNSATURATED CYCLIC SULFONES

The second type of sulfur dioxide-unsaturated hydrocarbon reaction is shown by conjugated diolefins. By a typical 1,4-addition, sulfur dioxide adds to a conjugated diolefinic hydrocarbon to form an unsaturated cyclic sulfone. For example, butadiene and sulfur dioxide easily react to form butadiene sulfone, a compound which might be considered as a thiophene derivative, *i. e.*, a dihydro dioxythiophene, by the following reaction:



(*a*) *Preparation of Cyclic Sulfones.* In the synthesis of cyclic sulfones, the presence of peroxides or other catalysts for polysulfone formation must be avoided, or a polymerization reaction becomes dominant and a polysulfone forms:



Since unsaturated hydrocarbons usually contain peroxide impurities, it is common practice to add a small amount of hydroquinone or other antioxidant when preparing the cyclic sulfone. In the presence of an antioxidant, butadiene and sulfur dioxide form the cyclic sulfone on standing at room temperature for a few days or at 100° for several hours, the yields being 70–80 per cent in either case. The product is a colorless, crystalline solid melting at 65°, soluble in warm water, and insoluble in nonpolar organic liquids. Butadiene polysulfone, like the olefin polysulfone, is amorphous, insoluble, and melts with decomposition over a wide range around 200°.

(*b*) *Chemical Behavior of the Cyclic Sulfones.* The most interesting chemical property of these cyclic sulfones is their thermal dissociation to regenerate the diolefin and sulfur dioxide. Butadiene sulfone, for example, smoothly dissociates on heating at about 120° into butadiene and sulfur dioxide, the yield of butadiene being of the order of 90 per cent. On the basis of this property there are several patented processes for separating hydrocarbon mixtures of narrow boiling range. A C_4 fraction containing *n*-butane, butylenes, and butadiene is formed by the catalytic dehydrogenation of *n*-butane in the manufacture of butadiene. Treatment of this mixture with sulfur dioxide in the presence of an antioxidant yields butadiene sulfone and unreacted butane and butylenes. Extraction with warm water dissolves only the sulfone, and the butane and butylenes are recycled to the dehydrogenation unit. In the last step the sulfone is recovered by evaporation of the water solution, decomposed to butadiene and sulfur dioxide, and the sulfur dioxide removed by washing with water or alkali. Figure 2 outlines this process step by step on the next page.

Instead of washing with water to remove sulfur dioxide in the last step, a molten sulfone is proposed as a

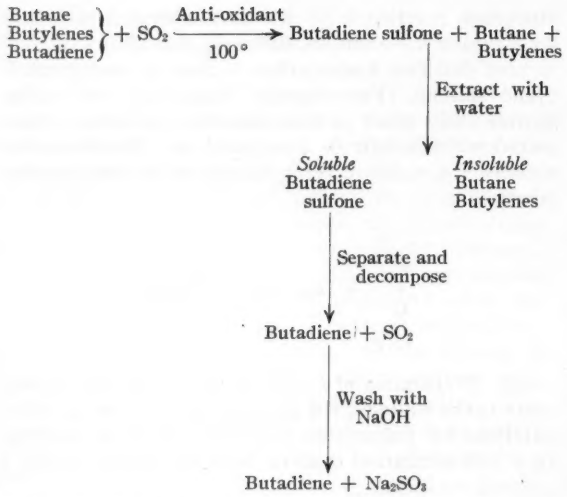


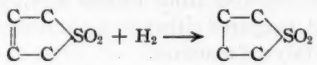
FIGURE 2.—SEPARATION OF BUTADIENE FROM A C_4 FRACTION

better solvent. A 1:1 mixture of butadiene and isoprene sulfones melts at 28° and will dissolve 37 per cent of its weight of sulfur dioxide at 28°, 95 per cent at 10°. Water at 0° dissolves only 23 per cent of sulfur dioxide. Furthermore, the recovery of sulfur dioxide by heating the solutions is greater when the solvent consists of sulfones.

This process of separating a conjugated diolefin from hydrocarbon mixtures can be applied to a C_5 cut to obtain isoprene or piperylene. If the sulfone is purified by one or more crystallizations from water, the purity of the diolefin obtained by decomposition will be high. In fact, this constitutes one of the best methods of purifying a conjugated diolefin.

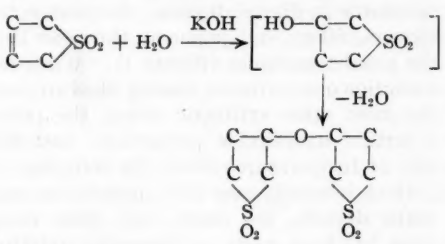
This process suggested to us the possibility of separating a drying oil into one fraction consisting of glycerides having one or more pairs of conjugated double bonds and a second fraction consisting of nonconjugated and saturated glycerides. It is well known that dehydrated castor oil contains about 30 per cent of conjugated molecules and about 70 per cent of nonconjugated. An increase in the concentration of conjugated molecules would improve both drying and film properties. A separation of a commercial sample of dehydrated castor oil was attempted by allowing it to react at 100° with excess sulfur dioxide so as to form sulfones of the molecules containing conjugated bonds. It was expected that the polar nature of these sulfones would allow their extraction by alcohol and subsequent decomposition of the sulfones would yield the desired oil. Unfortunately, these conjugated molecules do not form sulfones as do the simple diolefins—butadiene and isoprene, for example. Further studies showed that unsubstituted diolefinic hydrocarbons of six carbon atoms or more, in which neither double bond is at the end of the chain, either do not form cyclic sulfones at all or give yields of only a few per cent. This reduced activity in the addition of sulfur dioxide may be the result of steric hindrance provided by the groups attached to the butadiene nucleus.

The cyclic sulfones show many addition reactions because of the presence of a reactive olefinic double bond. Hydrogen, halogens, halogen acids, and many other reagents will add to the sulfones. In the presence of nickel or platinum catalysts, hydrogen at 20–30 pounds pressure readily hydrogenates the double bond of butadiene sulfone, but does not affect the sulfone group as can be seen in the following equation:

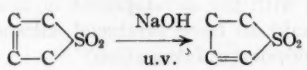


The product is a fairly stable, high boiling liquid (150° at 15 mm.), sometimes referred to as butadiene sulfolane. The sulfolanes possess very interesting solvent properties. As extraction solvents, they might be viewed as less polar modifications of liquid sulfur dioxide, which therefore have greater solvency for organic substances but still retain water-solubility. Recent patents propose the sulfolanes as solvents to extract aromatic hydrocarbons from mixtures with naphthenes and paraffins, for refining lubricating oils, for removing dark-colored substances from tall oil, and for separating drying oils into more and less unsaturated fractions.

In the presence of aqueous potassium hydroxide the units of water add to butadiene sulfone with remarkable ease to form an unstable alcohol derivative which spontaneously undergoes dehydration to an ether:

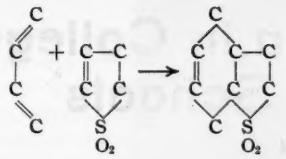


A tautomeric rearrangement occurs in the presence of alkali and ultraviolet light to form the α-butadiene sulfone



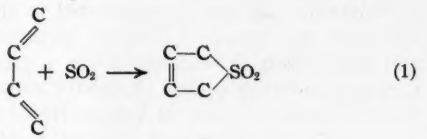
in which the double bond is now conjugated with respect to the sulfone group. The resulting activation of the double bond, comparable to that in α,β-unsaturated carbonyl compounds, is sufficient to give this substance dienophilic properties, and by 1,4-addition to butadiene a bicyclic sulfone is formed according to the reaction at the top of the next page.

These reactions of the cyclic sulfones illustrate their active chemical character and suggest many excellent possibilities in organic synthesis.

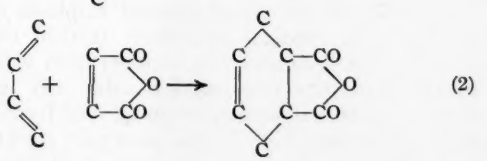


A COMPARISON OF THE CYCLIC SULFONE AND DIELS-ALDER REACTIONS

In several respects the formation of the cyclic sulfones and Diels-Alder reactions, such as the addition of maleic anhydride to butadiene, show a marked similarity:



(1)



(2)

Both reactions proceed through 1,4-addition to a conjugated diolefin with the formation of cyclic products. The reactivity of a diolefin with respect to sulfur dioxide and maleic anhydride is a function of its structure and configuration. Because of one or both of these factors certain diolefins react with neither sulfur dioxide nor maleic anhydride, according to equations (1) and (2), while other diolefins will enter the Diels-Alder reaction but will not form a cyclic sulfone. At the present time the Diels-Alder reaction appears to be very much more general.

Both the cyclic sulfone and many Diels-Alder reactions are reversible, and the adducts dissociate on heating to give the original reactants. As a rule, the sulfones are more readily decomposed, temperatures of 200° or less being effective. As pointed out before, conjugated diolefins will interpolymerize with sulfur dioxide to yield polysulfones, if an antioxidant is not present. Likewise, the reactants for a Diels-Alder reaction in certain cases will yield polymeric products instead of the simple adduct. In general, this alternative route of polymerization is more likely to be followed in the case of the sulfone reactions.

Certain nonconjugated diolefins react with maleic anhydride to form adducts whose structure shows that isomerization of the double bonds to conjugated positions occurred prior to or during addition, suggesting that the presence of maleic anhydride is conducive to isomerization. Whether sulfur dioxide exacts a similar effect can only be inferred from the patent literature which contains at least one reference to a process for isomerizing nonconjugated drying oils to conjugated oils by heating with liquid sulfur dioxide under pressure.

Finally, the electronic mechanism proposed for the Diels-Alder reaction is equally applicable to the formation of cyclic sulfones. This simply means that the opening of the carbon-carbon double bond for the addition of maleic anhydride and the increase of the sulfur valence from four to six for the addition of sulfur dioxide are equivalent in terms of electrons.

This, briefly, shows the common basis for these two reactions. Since Diels-Alder reactions have been much more extensively studied, comparisons such as these are helpful in anticipating and plotting the course of future research on the cyclic sulfones.

As far as we know, there are no direct applications of these sulfones to coating compositions. Sulfur dioxide has two uses, however, which are closely related to these sulfone-forming reactions. For the thermal polymerization (heat-bodying) of drying oils, sulfur dioxide is a catalyst—*i. e.*, when bubbled through an oil heated at 290–300°, it reduces the time required to reach a given viscosity. In the second process, referred to earlier, sulfur dioxide is claimed to bring about the shifting of isolated double bonds to conjugated positions in an oil heated with sulfur dioxide under pressure at about 200°. In neither the catalytic polymerization nor the isomerization process are sulfones formed as final products, but it seems likely that they might be unstable intermediates, whose formation and decomposition open and reform carbon-carbon double bonds so that polymerization and isomerization reactions involving these double bonds proceed more readily.

SUMMARY

Sulfur dioxide reacts with unsaturated hydrocarbons and their derivatives to form thermoplastic, resinous polysulfones. The reaction conditions for this polymerization, the structure, physical and chemical properties of the polysulfones have been described. With conjugated diolefins sulfur dioxide adds to form unsaturated cyclic sulfones in a reaction comparable in several respects to the Diels-Alder reaction. This addition is reversible and it is therefore useful in separating hydrocarbon mixtures and in purifying diolefins. The cyclic sulfones are reactive compounds useful for the preparation of solvents and many other derivatives. Neither the polysulfones nor the cyclic sulfones appear to have found any large practical application, but both substances offer excellent possibilities.

LITERATURE CITED

Material for this paper was taken from the patent literature and the following references:

(1) BACKER, H. J., J. STRATING, AND L. H. H. HUISMAN, *Rec. trav. chim.*, **60**, 381 (1941) and earlier papers.
(2) GILMAN, H., "Organic Chemistry," John Wiley and Sons, Inc., New York, 2nd Ed., **1943**, Vol. I, pp. 765, 873.
(3) MARVEL, C. S., AND W. H. SHARKEY, *J. Org. Chem.*, **9**, 113 (1944) and earlier papers.
(4) NORTON, J. A., *Chem. Revs.*, **31**, 319 (1942).
(5) SNOW, R. D., AND F. E. FREY, *J. Am. Chem. Soc.*, **65**, 2417 (1943) and earlier papers.
(6) SUTER, C. M., "Organic Chemistry of Sulfur," John Wiley and Sons., Inc., New York, **1944**, chap. VII.

Comparison of Instruction in Colleges and Military Service Schools[1]

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THE usual high-school and college instructional programs have been characterized by terms of semesters covering from 16 to 20 weeks. Instructors and administrative personnel at such institutions have been amazed at the intensified specialized military training programs conducted in Army Service Force Schools in which courses of instruction were completed in periods of from ten days to several weeks. Practices used in such service schools have points which may be of value to the older, more stable, institutional instruction. In turn, it cannot be said that the principles and practices used in the service schools have been without fault or above criticism.

Army Service Schools in operation during World War II fell into the following three classes: (*a*) schools for noncommissioned officers, (*b*) officer candidate schools, and (*c*) officers' schools. The staffs and faculties of such schools were composed of regular army officers, reserve officers, officer candidate school graduates, and selected noncommissioned officers.

With the successful conclusion of combat in World War II, it is possible to draw an unbiased comparison between instruction at the college level and in military service schools with regard to (*a*) emphasis on subject matter, (*b*) selection of instructors, (*c*) consideration of instructors' backgrounds and previous training, (*d*) supervision of instructional methods and techniques, (*e*) composition and interest of student body, and (*f*) use of visual aids and classroom helps for instruction. Each of these items will be briefly discussed by the author, who has had eleven years' experience teaching chemistry at a state university, and thirty months of wartime experience as an officer on the staff of the officers' division of the Chemical Warfare School at Edgewood Arsenal, Maryland. While the details of the organization and the operation of the various service schools varied, the general statements mentioned below concerning one school may be considered as typical of such installations.

It must be remembered that the United States was converted from a peacetime basis to full-scale war production in a very short time. Service schools which were in existence prior to the war were also expanded manyfold in a very short time. Errors in policy and judgment were inevitable but, when recognized, were immediately corrected. A competitive spirit existed among the several service schools, with all sharing any new instructional ideas which would enable students to absorb more material in a shorter time.

In the average college course a broad general viewpoint has always been stressed. Topics have been discussed from a historical point of view and fundamental concepts thoroughly covered. In the physical sciences considerable time has been devoted to the theoretical approach to topics. Chemical structure, formulas, and mechanism of reactions cover a great portion of time and space in college chemistry courses. In contrast, a course in Chemical Agents offered at the Chemical Warfare School placed greatest emphasis on field identification, physical properties, tactical use, and protection of personnel and matériel from war gases. Factual information of practical value only was presented. Chemical names, symbols, and formulas, as well as structure, were for the most part intentionally and completely avoided. All courses of instruction at service schools stressed only the real "battle value" of subject matter. Other associated facts were either subordinated or completely ignored. Thus, it readily becomes apparent that such an approach to a subject materially reduced the instructional time required and correspondingly shortened the length of the courses.

College instructors are generally selected for a position after having had several years' teaching experience during the time usually devoted to study for advanced degrees. Likewise, a college instructor is frequently engaged in some sort of research work allied to his topic of instruction. Thus, his knowledge of the subject extends well beyond the immediate text at hand.

Instructors in service schools were composed of (*a*) regular army officers, (*b*) reserve officers, (*c*) officer candidate school graduates, and (*d*) selected enlisted men. The regular army officers were fully familiar with the subject matter as well as the courses of instruction, while the reserve officers were usually professional men in civil life (relatively few chemists were used as instructors at the Chemical Warfare School), who were required to attend a "school" before being placed on its staff. In some cases, the instructor so prepared was not too familiar with the subject matter. One specific instance will illustrate lack of consideration of a man's background with his assigned position on the staff of the Chemical Warfare School. A man who was a flour blender in a flour mill in civil life was directed to be an instructor in chemical agents when he had graduated from a school, while another officer who had three degrees in chemistry and who had been teaching chemistry for several years was designated as a camouflage and security instructor. Few instructors in service schools had been teachers in civil life. All instructors were required to attend a short course (20 to 50 hours)

[1] Contribution #580 from the Department of Chemistry, The University of Pittsburgh.

in "the mechanism of instruction." It is readily understood that the rapid expansion of the military program did not provide time for an elaborate extensive instructor-training program. The officer candidate graduates and noncommissioned officers selected as instructors in service schools were very intelligent and were selected from among the leaders in their respective groups and classes. Though their backgrounds were varied, and relatively few were college graduates, for the most part they have proved themselves both willing and successful instructors.

As the war progressed, returning officers and men with battle experience were added to the faculty of the service schools. These men were able to supplement specific phases of classroom instruction with personal battle experiences. Likewise, reports from various theaters of operation, giving up-to-the-minute information and recent trends in battle techniques, were made available for the school staffs to review and incorporate into instructional periods. This item may be compared with current events and recent research developments which are incorporated into certain phases of high-school and college instruction. Such items as the actual details of a specific amphibious operation involving the use of a chemical smoke screen added new battle reality to previously theoretical and maneuver discussions of the use of chemical smoke in landing operations.

Executive officers of the service schools made a practice of visiting classrooms as well as field instruction for the purpose of observing the instructional procedure. In addition, a so-called "supervisory" branch of the school had personnel whose duty consisted of visiting classes with the idea of improvement of instruction. In many cases these supervisors were able to observe slight mannerisms of which the instructor was quite ignorant. In one case the instructor continually fingered a piece of chalk, occasionally tossing it into the air and catching it. In another case the instructor's presentation was continually broken by the unnecessary use of the word "and." Such details, though minor in nature, when corrected, improved the caliber of the instruction. Other, more serious, teaching errors were observed and corrected as a result of supervisory staff visits.

Some of our college departments make a practice of having full-time instructors visit classes of the more inexperienced graduate students who are part-time teachers. Other college departments do not check on their inexperienced instructors. Constructive criticism offered by fellow members of a particular staff would do much to keep our college instruction at a peak level of efficiency.

The service schools had elaborate "lesson plans" covering each period of instruction, either in the classroom or out in the field. These were prepared by experienced instructors and were intended as models to be followed by other instructors who might be required to present the individual periods at future times. These "lesson plans" were broken down into time budgets accurate to intervals of one minute. It was intended that a new instructor would be able to review a lesson plan and, with this as his guide, would then be able to present any period in the school curriculum. All experienced instructors know that mere repetition of words without personal contact and enthusiasm does not result in a satisfactory presentation. The individual himself must enter into successful instructional presentations. No two men will say the same words and devote exactly the same number of minutes to any specific topic. This phase of service school instruction tended to mechanize the instructional program and detract from the presentation due to removal of the individuality and personality of the instructor. In many cases a new instructor taking over a period previously presented by another individual rewrote the lesson plan, abiding by the general principles of the period, but inserting his own time budget and word choice.

Service school supervisors stressed the need for student participation in all classes. An unwritten rule adhered to was: "At least an average of one question from the platform each five minutes." Men in uniform are no different from civilians in that a long lecture tends to put them to sleep. No officers' class was permitted to last more than fifty minutes without a ten-minute break, while enlisted men's classes usually had a "stretch" every twenty-five minutes. These policies reduced the number of "sleepers" and aided in maintaining interest.

The lecture form of instruction was definitely discouraged in service school teaching. Conferences, classroom exercises (graded or ungraded), demonstrations, training films, and field exercises with student participation, in so far as possible, were favored. No period was to be concluded without giving students an opportunity to raise questions related to the material presented. Each period (conference type) ended with a brief summary of the material presented. This summary could be (*a*) given from the platform, or (*b*) given as oral answers by the students to questions raised from the instructor in charge. In some cases the summary took the form of a short answer type of quiz. Papers were collected and graded.

Since many classes were held out of doors as "field exercises" or "demonstrations," it was necessary to have those concluding summaries in the field. These were called "critiques." Again student participation was stressed, with the instructor in charge leading the critique by employing a sound psychological approach. At the beginning the instructor commended the class and specific individuals on particular phases of the operation which they carried out well, and then called on specific students for ideas as to where and how the exercise or demonstration could have been improved. At the conclusion he would point out specific cases where the exercise was weak and where obvious errors in judgment and maneuver had been made by students. The policy of "commend first and follow by critical discussion of details" had a very favorable effect on the

students. It is human nature to appreciate commendation. Instructors who stressed bad points and neglected to mention the good points in a field exercise were not in good favor with the students.

Examinations, previously approved as to fairness of wording and content by the supervisory branch, were administered after the completion of the study of a topic. Students received three possible letter grades: "EX" (excellent), numerical grade 86–100; "S" (satisfactory), numerical grade 70–85; and "U" (unsatisfactory), below 70 on the numerical scale. When enrolling in a course each student was given a number, which was recorded opposite his name in the personnel records section of the school. All examinations and graded exercises were marked by the student with his assigned number in lieu of his name. The instructor graded all papers on the basis of 100 per cent as being perfect, and prepared a list of student numbers with only letter grades opposite. This list was posted on the bulletin board in each classroom. Thus, those students who failed an examination or exercise were not embarrassed by having their names and grades posted before the entire class. Graded papers were *never* returned to students, but in the event a student desired to observe where he had difficulty on a paper, the instructor would meet with him at a convenient time and the two would review the grading system. A second list of grades, showing student numbers, numerical and letter grades, was forwarded to the personnel secretary for incorporation into the student's record. At no time was the instructor permitted to learn the number of any student in a class.

Certificates were issued following a "graduation" exercise on the termination of each service school. These certificates listed the various subjects in which the student had received instruction, as well as the number of class hours devoted to each subject. In the event that a student passed all subjects except one, such as "general tactics," he would be given a certificate which was "red-lined," meaning that a red ink line was drawn through the subject or subjects which he failed. No definite policy was established, though three or more red lines were generally considered sufficient for withholding a certificate from a student. In this event a letter was sent forward to his permanent station stating that he had not received a certificate due to low academic standing.

The red-lining procedure of the Army Service Force Schools may be considered as the equivalent of a college student failing in a specific subject. Excessive failures in college are considered sufficient grounds for dismissing the student from school. Service Force School policy was very similar in this respect. In college, a student who fails a single subject is customarily given an opportunity for repeating the subject in subsequent terms. This was impossible in the case of such failure in service schools.

In college instruction, examination papers are usually returned to the students and the examination discussed by the entire class. Since students who fail an examination have their papers before them during such discussions, there is often lack of interest as well as embarrassment associated with such class meetings. In service school discussions of examination questions neither the instructor nor the student body knew the names of the students who had failed. In this manner it was possible to discuss erroneous answers with a minimum of personal contact or individually directed remarks.

A Chemical Warfare School staff member was designated as "Course Director" for each class attending the officers' division of the school. His duties, in addition to instruction, consisted of advising students regarding routine announcements, schedule changes and other administrative matters. After a particular class had been graduated, the course director prepared a brief report for each student. This report was forwarded to Washington and included brief statements relative to (*a*) the general efficiency of the student, (*b*) a suggested military assignment, and (*c*) a statement regarding the value of the man to the service. Information for these reports was obtained from personnel record files, past experience of each man, grades attained while attending school, and interviews with, as well as observation of, students in class. The duties of a course director may thus be considered similar to those of a college placement bureau. It is quite true that service school graduates were not concerned with the "hiring problem" which characterizes college graduates, but information which would assist in placing a graduate in a position where he would be of maximum value to the country was considered very vital.

In civil life, as a student progresses from high school on to college, he automatically passes a screening process in which his weaker and less interested friends drop out. Both interest and intellect usually increase as one advances to institutions of higher learning. Likewise, college students have generally selected their courses of instruction as a result of personal interest and desire.

In service schools the student bodies were selected as a result of specific allocations to various areas, camps, and stations throughout the country. Military personnel in these areas who decided to attend schools had opportunities to indicate preferences for any of the several possible schools and, if qualified in the eyes of their respective commanding officers, were recommended for particular schools. In some cases an individual who was interested in attending one school was sent to another in which he had but little interest. The result of such a system of selection was a heterogeneous group of individuals with varied backgrounds, training, experiences, and interests. One typical class at the Chemical Warfare School, Officers' Division, contained students who in civil life had been (*a*) radio and stage singers, (*b*) lawyers, (*c*) railroad men, (*d*) chemists, (*e*) salesmen, (*f*) telegraph operators, (*g*) teachers, and (*h*) manufacturing men. It is readily seen that instructional problems encountered with such

a heterogeneous group would be far greater than those in the average college class.

Subjects requiring a knowledge of simple arithmetic, such as company administration, supply and logistics, and map reading, were baffling to many students. Memorization and repetition of factual details often tended to replace rational thought processes in many such subjects.

The above situations, combined with rare cases in which uninterested students were sent to schools, and other cases in which students were sent to specific schools via political or other means, produced instructional problems seldom encountered in college programs.

The instructional and visual aids used in service schools were most elaborate and of very great assistance in all teaching. Film bulletins and training films were being produced throughout the course of the war. These attempted to keep up with current changes in matériel as well as battle tactics and techniques. Wall charts were used in conjunction with practically all class periods. Sand tables as well as sectionalized models were used whenever possible. Students were often taken into the field to observe a unit of specially trained troops demonstrate a particular operation. In other exercises, certain students acted as demonstrators while the remainder of the class observed. Sound recordings of battle noises played over a public address system substituted for the use of firearms and weapons. Blank and training ammunition was used in many exercises. In brief, any material which could be used to impart greater realism to all phases of training was used very profitably. In general, students were permitted to view films showing the operation as well as discuss a particular piece of equipment before going into the field for first-hand tactical contact with it. In this manner the field exercise may be considered as the laboratory experiment for students in service schools. In service schools as well as in colleges, it has been definitely demonstrated that the student learns more about an item or principle by means of first-hand contact (experiments) than he does by merely reading texts or listening to someone tell him about them.

Military textbooks (field manuals and technical manuals) are best characterized by brief, accurate statements which are considered as being "heavy" reading. Basic Field Manual FM 21-5 entitled "Military Training" (July, 1941) contains eighty printed pages filled with vital truth and factual information related to instructional methods and teaching procedures. It does not contain any sketches or cuts and is very weighty reading. More recently, TM 21-250, entitled "Army Instruction" (April, 1943), has been published. It contains essentially the same fundamental material as is present in FM 21-5 presented in a more realistic as well as detailed manner.

Six steps to be used in instruction are stressed in both of these military manuals. They are: (1) preparation, (2) explanation, (3) demonstration, (4) application, (5) examination, and (6) discussion. These six steps are very vital and can be properly applied, with some modification, to teaching any type of subject matter. The "preparation" stage is to be carried out by the instructor prior to meeting the class. He presents the material in the "explanation" and "demonstration" steps, while student "application" and "examination" performance give him the necessary information to be covered in the final "discussion" stage. These steps are not new, but should be evident in some form in all satisfactory and successful instructional procedures, regardless of civil or military school systems.

In conclusion, it may be stated that under the circumstances of a very rapid expansion and the demands of rapid turnover of properly trained graduates with a specific job to be filled, the service schools have done a very fine job. Selection of staff members, methods of classroom supervision, and consideration of the desires and attitudes of students have not always been ideal or comparable with those evident in college programs. Training aids and progressive changes in service school instruction were superior to many of those in college academic training. The service school system used in grading papers has advantages over older systems. In the selection of instructors, as was the case in the selection of students, the individual was given little opportunity to indicate a preference for certain topics, but was merely assigned to a specific branch as an in-instructor, or school as a student, regardless of his background.

Learning is naturally a slow process which entails time. There is no known short cut to thorough knowledge and understanding. Accelerated military programs gave a series of situation-action examples which filled an urgent need during a vital period. It is doubtful if much of the factual information gained by students in service schools will be retained for any appreciable time after their separation from the service. On the other hand, thoroughly indoctrinated fundamental laws and principles taught in basic college courses are often retained and used throughout a graduate's after life.

"....As in 1918, so in 1945, the main strength of the I. G. lies not in their factories. To destroy an enemy's factories often proves in the long run to his advantage. He rebuilds them better. It is the human element, the team, and the accumulated technical knowledge that counts. Money you must have in quantity, but it must be educated money, using science and technology with great judgment...."—Dr. Herbert Levinstein

Construction of a Fractionating Column

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ONE of the most important chemical laboratory operations is the separation of compounds by distillation. In recent years efficient fractionating columns have become standard equipment in organic research laboratories, both academic and industrial. Although construction of efficient, dependable, inexpensive, general-purpose columns for use under both atmospheric and reduced pressures is actually a simple process, nevertheless an inexperienced worker is seriously handicapped by the lack of adequate step-by-step descriptions in the literature.

The present paper describes in detail the method for the construction of a simple, inexpensive, all-purpose column which, in the authors' opinions, combines the best features of several different types previously reported, and which has been found to give excellent results. These directions should prove particularly useful to workers who do not have available the funds to purchase commercially built columns. For one who has not previously used or built a similar piece of apparatus, many of the techniques described should save both time and equipment which otherwise would be lost in their discovery.

The parts necessary for construction of the column are:

1. A pyrex glass column 30–35 mm. in diameter ($1^3/_{16}$–$1^3/_8$ inches) or less if the column is not intended for use under greatly reduced pressures, and of desired length (the columns regularly used by the authors are 4–5 feet in length).
2. Two pyrex glass tubes, one 50 mm. in diameter, (2 inches), and the other 60 mm. ($2^3/_8$ inches) equal in length and several inches shorter than the column (see diagrams).
3. About 50 feet of 22 gage (B. and S.) nichrome or chromel resistance wire.
4. A 360° thermometer.
5. Several feet each of $^1/_2$- and 1-inch asbestos tape.
6. About $^1/_2$ liter of water glass.
7. Two 3-foot lengths of standard 2-inch[1] magnesia pipe wrapping.
8. Three feet of metal stripping used to mount magnesia-wrapped pipes.
9. A Variac[2] or Varitran[3] transformer for control of the temperature of the nichrome-wrapped jacket.
10. Packing sufficient to fill the column (berl saddles[4] or case-hardened, triple-turn glass helices are recommended for distillations conducted under low pressures; single-turn glass[3] or stainless steel[3] helices, one-eighth the diameter of the column, for work at atmospheric or somewhat reduced pressures).
11. Two ordinary clamps and clamp holders and an iron ring stand of sufficient height to mount the column. Precise control of the temperature of the distilling pot may be assured by use of a Glas-Col heating mantle[3] with an additional transformer.

FIGURE 1.

FIGURE 2.

FIGURE 3.

DIRECTIONS FOR ASSEMBLING COLUMN

Figure 1. A column of the type shown, 30–35 mm.

[1] So called because it is regularly used to cover pipe of 2-inch inner diameter; actual inner diameter of the wrapping is just under $2^1/_2$ inches.

[2] Obtainable from General Radio Company, 275 Massachusetts Ave., Cambridge, Mass.

[3] Obtainable from Scientific Glass Apparatus Company, Bloomfield, N. J.

[4] Obtainable from Maurice Knight, Kelly Ave., Akron, Ohio.

($1^3/_{16}$–$1^3/_8$ inches) in diameter and equipped with ground-glass joints, is used. The perforated glass bulb serves to hold the packing in the column and to prevent flooding. A 360° thermometer is mounted midway on the outside of the column by means of $^1/_2$-inch asbestos tape cemented with water glass. If the column is to be used at temperatures in excess of 360°, a thermocouple may be substituted for the thermometer.

Figure 2. One-inch asbestos tape is wound around the ends of the column until a wrapping of the same diameter as the inner diameter of the inner glass jacket is obtained. Water glass is applied generously to the asbestos tape, which then dries to give a rigid structure. The wrappings are spaced at each end of the column so that, if the two glass jackets are of proper length, exactly $^1/_2$ inch of the wrapping protrudes from each end when the jackets are slipped into place.

Figure 3. The 50-mm. (2-inch) pyrex tube which is to serve as the inner glass jacket is cut to proper length for assembly. Two holes are blown or pulled out, one at each end. The jacket is then fitted with two strips of $^1/_2$-inch asbestos tape, which are cemented on opposite sides of the jacket over its entire length and serve to hold the resistance wire in place. The wire (as previously specified) is now wound about this jacket. Proper spacing of the turns is determined by the temperature range at which the column is to be operated. One-half inch spacings are satisfactory for temperatures up to 500°.

Figure 4. Winding of the resistance wire about the first glass jacket is accomplished simply with uniform spacing as follows: Both ends of the tube are fitted with rubber stoppers through which large cork borers have been thrust about halfway. The protruding ends of the cork borers are placed loosely in clamps supported by a pair of ring stands (4*a*). With such an arrangement, the wire may be wound about the jacket by rotation of the tube and spaced uniformly as desired with each revolution (4*b*).

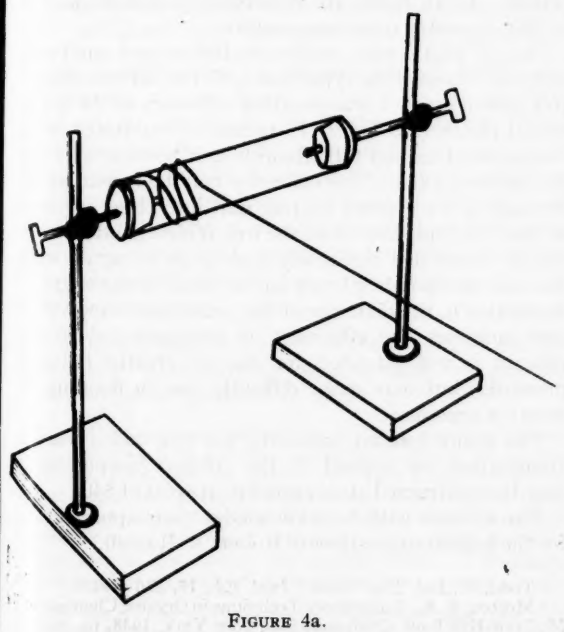


FIGURE 4a.

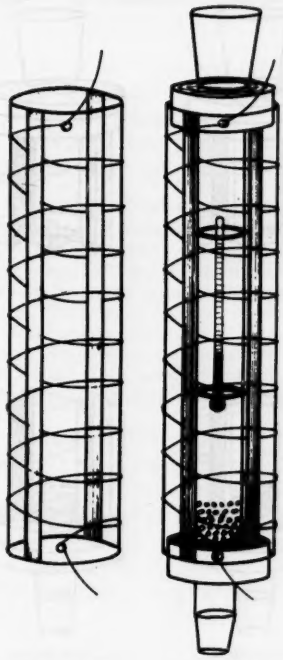


FIGURE 4b.

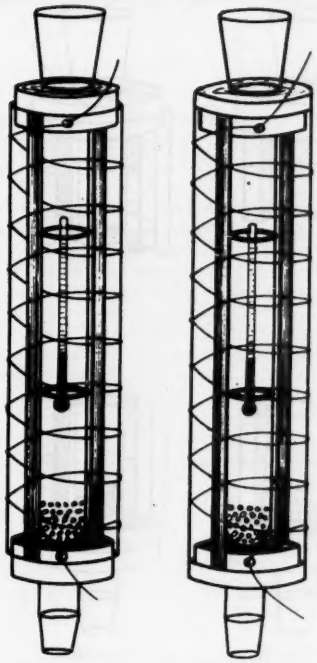


FIGURE 5.

FIGURE 6.

Figure 5. The first glass jacket is slipped into place over the asbestos wrapping. To facilitate this process, the wrapping at the lower end of the column should fit loosely and should be left loose to give a small degree of leeway to the column. This greatly decreases the likelihood that the lower ground glass joint of the column will be snapped off while the column is in use. The upper wrapping should fit snugly to give ample support. The two ends of the wire are run through the holes in the ends of the glass jacket and out between the asbestos wrapping and the first glass jacket.

Figure 6. The protruding asbestos wrapping ($^1/_2$ inch at both ends) is built up to the outer diameter of the glass jacket by wrapping with $^1/_2$-inch asbestos tape.

Figure 7. The ends of the first glass jacket ($^1/_2$ inch of glass jacket and $^1/_2$ inch of protruding asbestos tape) are wrapped with 1-inch asbestos tape until a wrapping of the same diameter as the inner diameter of the outer glass jacket is obtained.

Figure 8. The outer glass jacket is slipped into place over the asbestos wrapping; it should fit snugly at both ends.

Figure 9. The protruding asbestos wrapping ($^1/_2$ inch) at both ends of the outer glass jacket is built up with $^1/_2$-inch asbestos tape to a diameter slightly greater than the outer diameter of this jacket so that the tape

FIGURE 7.

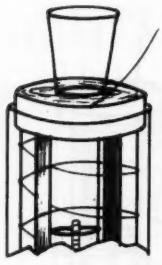


FIGURE 8.

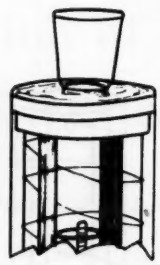
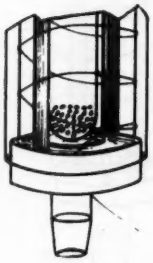
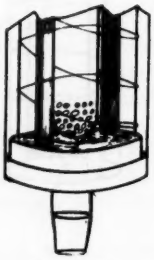


FIGURE 9.





will fit snugly in the 2-inch magnesia pipe wrapping.

Figure 10. Magnesia pipe wrapping (2-inch) is slipped over the outer jacket. Two 3-foot lengths of this wrapping are cut to proper length and connected by cementing together the cloth ends of the wrapping with water glass. A 4-inch wide strip of convenient length is cut from the magnesia wrapping to serve as a window for reading the thermometer and observing column operation. The removed strip, if treated generously with water glass and wrapped with cloth, maintains its shape and may be used as a door for the opening.

For mounting the finished column on a ring stand, the following clamps have been found completely satisfactory: an ordinary clamp is disassembled to give a rod with a bolt fitting. A proper length of metal mounting stripping is fashioned so that it fits uniformly and snugly about the magnesia wrapping (with the column within). A bolt is placed through the proper holes in the metal stripping and the hole in the rod, and the stripping is bolted tightly (so that the column does not slip) in the proper position about the magnesia with washers and nuts. One of these clamps at each end gives sufficient support for the column.

The authors have constructed a number of columns as described and have found the asbestos tape-water glass wrapping highly satisfactory. It is easily made and shaped, and sets to a tough binding in about 24 hours. The wrapping does not break away from the pyrex glass jackets when subjected to high temperatures, and columns constructed by its use have proved to be free from breakage when treated with ordinary care. It is intended especially for permanent assemblies; its removal, although possible, is time-consuming, and for this reason specially designed metal supports such as described by Todd[5] are recommended for columns which are to be dismantled frequently.

Any of the various types of total-condensation, variable take-off heads[6] may be used in conjunction with the column. The authors prefer the type illustrated (Figure 10). It is simple, compact, and inexpensive, and may be used without auxiliary attachments for distillation at atmospheric or reduced pressures. Hold-up of a carefully constructed still head of this type is less than 1 ml. An additional resistance-wire heating unit for the head may be necessary for high-boiling materials.

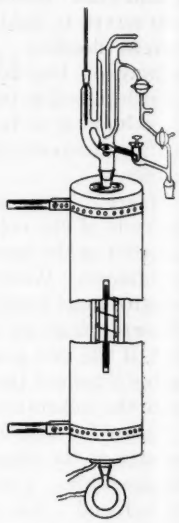


FIGURE 10.

Because of the relatively large diameter of the column and the ease with which adiabatic conditions may be insured, vacuum distillations may be conducted at pressures of less than 1 mm. without flooding. Normal hold-up in a 5-foot, 35-mm. diameter column, packed with berl saddles, is less than 15 ml. For high-temperature distillations the mounted thermometer may be replaced by a chromel-alumel thermocouple. Such an arrangement has the additional advantage that the column may be converted to a dehydration furnace simply by replacement of the packing with alumina pellets. 12–15 hours are required for an inner jacket at 300° to cool to room temperature.

Packed with 5-mm. single-turn helices and equipped with a still head of the type shown, a 5-foot 35-mm. diameter column gave a fractionating efficiency of 24 theoretical plates (2.5 H.E.T.P. inches) when tested with a mixture of carbon tetrachloride and benzene at a reflux ratio of 1:30. This efficiency may be increased by division of the column heating unit into three sections so that the temperature at the top, middle, and bottom can be controlled separately and made to agree with that at corresponding levels on the inside of the column. Reduction in the diameter of the packed column, which also increases the efficiency, is recommended if the column is not intended for use at greatly reduced pressures, but may cause difficulty due to flooding at very low pressures.

The entire column (including packing and a Variac transformer for control of the column temperature) may be constructed at an approximate cost of $40.

The authors wish to acknowledge their appreciation for the helpful suggestions of Robert R. Russell.

[5] Todd, F., *Ind. Eng. Chem., Anal. Ed.*, **17**, 175 (1945).

[6] Morton, A. A., "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Company, Inc., New York, **1938**, pp. 83–84.

Here and There in the Trade Literature[1]

THE best feature in the *Hercules Chemist* for October is "The seeing eye of spectroscopy," which is worth the time of anyone who is interested in this tool of the analytical chemist.

Several of the latest interesting developments in the Westinghouse Laboratories are described in the December *Westinghouse Newsfront*, including the gas turbine, high vacuum pumps, and the production of uranium.

The ridiculous heights to which the "atomic" myth has been carried are evident in the November *Esso Oilways*. A title catches the eye: "His discovery could wreck the world." On inspection it turns out to be a brief biographical sketch of John Dalton, the modern formulator of the Atomic Theory. It is more than a bit of a struggle to pass smoothly from this to the application of nucleonic energy. Of course, the atomic theory is the basis of *all* chemical developments and the great majority of the physical ones, whether it be nuclear fission, the synthesis of quinine, or the isolation of penicillin. Praise be to "the atom," the destroyer of empires!

The *Merck Review* for November has a nice illustrated account of the large-scale production of streptomycin, the new antibiotic.

"Oil through the ages" runs into its second installment in the December *Shell News*. This one carries the reader down through the first half of the nineteenth century, principally in the colorful oil towns of Pennsylvania. In the same number is a picture story of a geophysical party at work prospecting for oil by the seismographic method. The development and use of the "jellied gasoline" flame-thrower is also described.

The *Dow Diamond* for October tells about silicones, particularly the one known as DC 4, an oil remaining fluid to an extraordinarily low temperature, which permitted bombers to fly safely into the super-frigid stratosphere. There is also an interesting article on making charcoal and its use in the steel industry; and another on the use of magnesium anodes for the protection of pipes, etc., against underground corrosion. A simple explanation of the principles of electrolytic corrosion is given.

"Neoprene bounces ahead" in the December *DuPont Magazine*. The following explains nicely the position of the so-called synthetic rubbers:

> . . . Men have been "takers" for so many centuries—taking hides and wool from animals, taking fish from the sea, taking fruits and grain from the plant world—that it was difficult for many people even to conceive of a rubber which was not taken from rubber trees. Anything that resembled rubber but didn't come from trees, they thought could only be a rubber substitute.
>
> The fact of the matter was entirely different. Synthetic rubber is a new material, *like* rubber but *different* from it . . .

"The atom" comes in for another wallop, this time in the December *Beacon*. "Oil uses for the atom," is, however, a good general account of the beginnings of nucleonic energy, and is the first of two installments. It contains the following:

> When TNT explodes, the energy is evolved because the atoms present in the original TNT molecule rearrange themselves in new and stabler ways, making up new molecules with less available energy. The TNT bomb is, therefore, an "atomic bomb," because its energy is derived by rearranging atoms into combinations. The atomic bomb of recent history is, however, really a nuclear bomb, since its energy is not derived by rearranging whole atoms in new ways, but rather by rearranging the matter of the inmost part of the atom, the nucleus, into new forms, creating new nuclei and new and different atoms thereby.

The winter 1945 number of *Mechanical Topics* contains a lead article on the gas turbine which is worth reading for anyone wishing to keep up with the latest advances in power production. It is well summarized by the heading: "Made practical at last by metals that can handle its roaring red heat, the gas turbine offers lightness, compact simplicity, and high rotating speeds."

The following is quoted from the December *Industrial Bulletin* of Arthur D. Little, Inc.

COMPRESSION DISTILLATION

Most distillation is inherently wasteful of heat energy, for the liquid involved is usually boiled into a vapor and then condensed only to separate it from other materials. The liquid itself is at room temperature at both the beginning and the end of the operation, so that in principle almost all the heat consumed in distillation is recoverable. For many years engineers have been devising improved means for increasing this degree of heat recovery. Kleinschmidt compression distillation, the most recent step in this progress, follows a path different in principle from those previously explored, and was first used on a large scale during World War II, as a result of developments initiated in the laboratories of Arthur D. Little, Inc. The fuel consumption by this method is believed to be lower than by any other self-contained system of distillation.

In distilling sea water by the Kleinschmidt compression method, 175 or more pounds of distilled water may be obtained for each pound of fuel consumed, a ratio three to four times greater than with efficient conventional systems using fuel to generate heat. This low fuel consumption proved of great value to the armed forces during the war; thousands of Kleinschmidt compression stills were manufactured under license by E. B. Badger & Sons Company and used by the services. In the Navy, use of these stills to make fresh water from sea water released space normally given to fresh water storage and, for many types of vessels, extended the cruising range to an extent that was strategically important. The Army and Marine Corps used Kleinschmidt stills in land parties, particularly in desolate Pacific Islands. On Iwo Jima, for instance, the Marines continuously had fresh water from beachhead stills, although the Japs suffered desperately from its lack on this barren rock offering only a few useless hot sulfur springs. By the end of the war there was enough Kleinschmidt compression distillation equipment in service to produce pure distilled water for the daily needs of over a million men.

The principles of the Kleinschmidt compression distillation system were first publicly discussed recently before the American Society of Mechanical Engineers by Allen Latham, Jr., who headed wartime development of the method by Arthur D.

[1] For the company and address of a magazine cited, see THIS JOURNAL, January, 1946, pp. 38-39.

Little, Inc. The development was initiated before the war by a group headed by Dr. (later Commodore) R. V. Kleinschmidt, who is now again associated with Arthur D. Little, Inc.

In distillation, heat is consumed principally in converting a liquid to a vapor; this heat is later released when the vapor condenses back to a liquid. In the Kleinschmidt compression system, the heat released is recovered by using it to boil the incoming liquid. Under normal circumstances this would be impossible, since the vapor condenses at the same temperature at which the liquid boils and heat would not flow between them. In the Kleinschmidt system, however, the vapor from the boiling liquid is compressed, which raises its temperature several degrees. The properties of steam and other vapors are such that when compressed they will condense back to a liquid at a higher temperature than normally. In distilling sea water, for instance, steam, at three pounds per square inch gage pressure, condenses to water at about 222 °F., which allows enough temperature differential above the normal boiling point for the heat released by the condensing steam to flow to the raw water and boil it. In effect, the condensing vapor is used in place of externally supplied steam heat to boil the feed. No separate condenser or cooling water is needed.

Despite attempts to use the well-established principles involved in compression distillation, engineers did not consider it practical prior to the war; there were only a few specialized installations in Europe and none in the United States. Kleinschmidt compression distillation achieved widespread wartime use because early recognition of the value of the method led to inventions and a fruitful development program.

In conventional industrial distillation, the heat released by the condensing liquid is by no means thrown away. In the multiple-effect evaporator the condensing vapor from the first still, or "effect," is used to boil liquid in a second "effect," where a vacuum is maintained to cause the liquid to boil at a subnormal temperature. There may be a third, and possibly a fourth, effect with increasing vacuums, but additional ones beyond four have been found mechanically impractical. The Kleinschmidt compression system offers in practice the equivalent of about 15 effects.

The fuel economy of the Kleinschmidt distillation system is particularly valuable where waste steam is not available from other process operations. For instance, on diesel and gasoline propelled boats, such as fishing craft and small cargo vessels, the compression still, by replacing stored water, can release valuable space for cargo or fuel and increase cruising range substantially. In most distillation operations, the fact that the Kleinschmidt still does not use cooling water offers a definite saving, sometimes of critical importance. Compression distillation is, of course, applicable to liquids other than water, and in situations where the concentrated residue from distillation is desired rather than the distillate. For example condensed milk or maple syrup may be concentrated from the parent liquids at favorable low temperatures by compression distillation. With the wartime needs now satisfied, Kleinschmidt distillation equipment will be available to industry.

Out of the Editor's Basket

WE RECENTLY received from Professor A. B. Garrett, of the Ohio State University, a letter containing the following:

We have given placement tests in arithmetic for the past five years to all students taking general chemistry. The results of this test were so disturbing that the state department of education requested us to write an article for the *Ohio Schools Journal*. To do this, I enlisted the interest of Dr. Fawcett, who is director of the mathematics teachers' training at the Ohio State University. Upon publication of this article, the school authorities in the state became so alarmed that the state director of education issued an edict that a screening test be given to all high-school seniors in the fall of their senior year to be followed by a refresher course in arithmetic for all those who showed a deficiency. The results of this test have just been made known to the public and are so disturbing that the newspapers have taken up the issue and the governor has expressed himself in favor of a clean-up in this among all other areas showing such deficiencies. For the last three days the newspapers have been carrying headlines giving results of this test. I am enclosing a copy of one of the Columbus papers with such. If you care to use this, I think you will find it of interest to a number of chemistry teachers.

The article mentioned in the letter described the results of an arithmetic test given incoming students. In the course of the discussion, the following anecdote was told, which illustrates the whole point better than tables of data:

. . . Many high-school graduates who take positions in the world of business and industry cannot add fractions, solve a proportion, or convert fractions to decimals.

The extent of their understanding is well illustrated by the conversation between a war plant employee and one of the frequent inspectors from Washington. When requested to explain the nature of his work, the employee replied that it was his responsibility to cut from bars of metal a very thin strip. In response to further questions he stated that the thickness of this strip was one-ten thousandths of an inch. When the inspector wanted to be shown just about how thick that really was, he could get no satisfactory response. "Well," said the inspector, "if you cannot give me an approximate estimate of the thickness of this strip, tell me how many of them there are in an inch. "Oh, gee!" said the employee, "I don't know. There must be millions of 'em. . . ."

In commenting on the test and its results, a local newspaper, the *Columbus Citizen*, led off with the following:

Many Ohio high-school seniors are unable to do the work usually covered in the sixth and seventh grades.

This startling admission came today from the state director of education, Dr. Clyde Hissong.

Results of a mathematics test given to 2304 carefully selected high-school seniors from all parts of the state, Dr. Hissong, revealed, showed that:

Fifty-three per cent could not divide .75 into $25.20 and come up with the correct answer of $33.60.

Sixty-eight per cent could not figure that 62.4 equals 40 per cent of 156.

Seven per cent failed to identify the drawing of a circle.

Nineteen per cent failed to identify perpendicular lines.

Sixty-seven per cent could not answer this question correctly. "A man reports for work at 7:40 a. m. and leaves at 5:10 p. m. How many hours does he work if he takes one-half hour off for lunch?"

● It is now possible to isolate and recover by means of ion exchange processes certain important alkaloids which have been critically scarce during the war. An announcement stated that the rapidly expanding commercial application of ion exchange is giving the process an importance in the eyes of the chemist equal to

the techniques of distillation and solvent extraction.

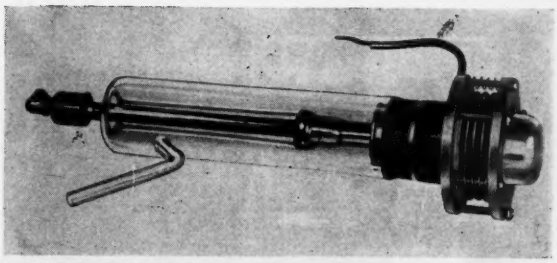
Methods have been devised recently for production of enzymes, hormones, vitamins, and other physiologically important substances. Synthetic exchangers, known as Amberlites, have been used in the processing of blood plasma, the isolation of amino acids, the demineralization of water for pharmaceutical purposes, the recovery of valuable tartrates from winery wastes and of copper from petroleum residues, the removal of formic acid from formaldehyde, the isolation of thiamin, and many other procedures. A method has also been developed for the isolation and recovery of such vital medicinal alkaloids as morphine, atropine, scopolamine, quinine, and quinidine. An instance of the latter is an installation at Brownsville, Texas, which was put into operation last year for the recovery of scopolamine from plants grown in the U. S. This drug, widely employed in medicine as a sedative, hypnotic, and mydriatic, and recently mentioned as an important preventive of motion sickness, was formerly obtained chiefly from Belgium, Hungary, Italy, and Yugoslavia. Since these sources were shut off by the war, it became vitally important to establish a native supply.

The success of the Brownsville project led to the adaptation of its methods by the U. S. Army, resulting in the development of a field process for the manufacture of antimalarials such as quinine by means of a portable unit which can be taken into the South American jungle areas where cinchona barks grow in large quantities. This eliminates almost insurmountable difficulties of transporting the crude bark through trackless wilds to processing plants sometimes thousands of miles away. The new ion exchange method permits the production of a ten grain dose at a cost of little more than three-tenths of a cent.

● Electrical sorting machines that hurl invisible atoms into a vacuum chamber and group them according to weight made possible the effective isolation of Uranium 235, the chain-reaction metal used in atomic bombs. Giant versions of the mass spectrometer, which sorts atoms in research and industrial laboratories, the devices detect the scarce U-235 which appears in natural uranium in a ratio of only one to 140, draw it away from its less-wanted atomic associates, and deposit it in special traps.

To Manhattan District Army Project engineers, the large number of these devices shipped to Oak Ridge, Tennessee, became "Calutrons"—a meaningless but adequate designation for a piece of secret equipment. Six months after University of California scientists, aided by Westinghouse research engineers, had completed paper plans for the Calutron, all development work had been completed and the units were being produced by some 800 workers, none of whom knew what he was making.

● The two-billion-dollar gamble of the atomic bomb project had to draw to many an inside straight in its race against time and the enemy. That it was successful in at least one of these can be laid to the curiosity



A NEW X-RAY TUBE, WHICH EMITS X-RADIATION FROM A HEMISPHERICAL WINDOW THROUGHOUT THE ENTIRE 180-DEGREE SOLID ANGLE WITH AN INTENSITY IN EXCESS OF FIVE MILLION ROENTGEN UNITS PER MINUTE, HAS BEEN PRODUCED EXPERIMENTALLY BY MACHLETT LABORATORIES, INC., OF SPRINGDALE, CONNECTICUT. A SMALLER VERSION OF THIS TUBE, PROVIDING OVER TWO MILLION ROENTGEN UNITS, IS ALREADY COMMERCIALLY AVAILABLE.

of a Westinghouse research scientist, working in the comparative obscurity of a small laboratory at the Westinghouse Lamp Division in Bloomfield, New Jersey.

The link that drew the two together was the urgent need for pure uranium. All other elements in the atomic project were available: money, manpower, laboratory facilities, and a backlog of research. Lacking only was a ready supply of pure uranium—or the time to produce it. It would take months for the plants then being erected to turn it out; and each day's delay meant postponement of the bomb's achievement and prolongation of the war.

This is where the scientific curiosity of Dr. Harvey Rentschler, Director of the Westinghouse Lamp Research Laboratories paid off. He had been producing pure uranium in small lots for many years before atom-splitting became a national program. In fact, all of the few tiny lumps of pure uranium available in America when the atomic project was started were produced in Dr. Rentschler's little laboratory.

He first hit the uranium trail after the close of World War I in search of a material that was superior to tungsten for lamp filaments. That the metal didn't work in this application was no deterrent to Dr. Rentschler. Using a crude but effective laboratory set-up, he continued to produce pure uranium a few ounces at a time —for further study and to supply the demands of scientific institutions who found this the one source of supply.

Then came the all-out atomic bomb program and the great need for uranium. The first experimental atomic-power generator, constructed at the University of Chicago and put into operation on December 2, 1942, used a thousand pounds of the precious metal in the "pile," all but a few hundred pounds of which came from the Rentschler-Marden process. It was probably one of the largest dividends ever paid on the scientific curiosity that marks the daily efforts of all men of research.

● An instrument which electronically measures the concentration of elements in alloys and automatically records the results has been developed by J. L. Saunder-

Courtesy of the Dow Chemical Company

DIRECT READING SPECTROMETER

son and coworkers at the Dow Chemical Company, Midland, Michigan. This direct-reading spectrometer, as it is called, has been in use in the company's magnesium alloying plant for several months, where alloy analyses can now be made in 40 seconds, a fraction of the time required when using the standard spectrograph. The substitution of an electronic method of measuring the intensity of spectrum lines eliminates the necessity for photographic and developing equipment and an expensive microphotometer, and avoids the errors commonly encountered due to film variation. Girl operators can be trained in a single day to use the instrument efficiently. The entire operation is fully automatic from the time the metal samples are placed in the instrument until the analysis is recorded on paper. Up to 14 elements can be determined simultaneously.

The development of the direct-reading spectrometer will be significant in all metal industries and in any chemical process where close and constant spectroscopic control is desirable. In melting, alloying, and casting of metals, it will lower costs by reducing the time a melt must be kept at temperature while waiting for analytical reports. Accuracy is equal or superior to that possible by spectrographic methods.

● The deleterious effect of the war on graduate research is made evident by an examination of figures representing the annual totals of doctoral dissertations accepted by American universities since 1941. These figures are brought out in *Doctoral Dissertations Accepted by American Universities* (No. 12, 1944–45, H. W. Wilson Company, **1945,** $1.50). In 1941 the number had reached the all-time high of 3526, but since then yearly totals have declined steadily and the figure for 1945 is 1576.

Sixty-two of the dissertations included in this year's list are designated as "secret war research." The practice of withholding information in the case of dissertations relating to war research has continued through the war years. Now that hostilities have ceased institutions may find it possible to release information hitherto kept secret and an effort will be made to obtain information on such items for inclusion in future volumes.

● Improved radio and television reception in postwar civilian sets is promised by carbonyl iron powder which was first made in this country in 1941. It is being specified by design engineers for use in civilian electrical, radio, television, and electronics equipment. During the war this product was considered so critical that reserve equipment was installed and is now available for the anticipated increase in civilian needs domestically and for export.

An announcement from the General Aniline & Film Corporation says, "Our Grasselli, N. J., plant is producing carbonyl iron powder in sufficient quantities to meet all civilian demands. The unusual magnetic and electrical properties of carbonyl iron powder make it ideal for use in manufacturing electromagnetic devices. Its use will permit forthcoming radio sets, both FM and AM, to give higher performance, especially improved tone quality, and will make possible sharper tuning. It will also provide a sharper television image. Throughout the war carbonyl iron powders were used in making radio equipment for planes, tanks, and ships, as well as in radar and various secret electronics devices."

● Spun-glass fabrics used by certain manufacturers to line women's sports clothing and babies' coats have been found to cause skin irritations, the U. S. Public Health Service has reported.

This finding resulted from an investigation of complaints received from purchasers of suits lined with glass cloth linings. In every instance, the garment had been returned to the dealer in Atlanta, Georgia, with the complaint that the wearer suffered dermatitis. The wholesaler asked the Public Health Service to investigate.

The Dermatoses Section of the Industrial Hygiene Division of the Public Health Service found that the skin condition was not a disease but rather a mechanical irritation caused by the suit lining. Spun-glass fabric had been intended for curtains and upholstery; however, with the scarcity of materials for linings, the manufacturers purchased the surplus from the Government to be used as a substitute.

● Silicone oils that flow at temperatures as low as 121 degrees below zero Fahrenheit without congealing have been developed by General Electric's Research Laboratory in Schenectady. These oils, prepared with methyl silicone polymers, will be useful as hydraulic fluids for aircraft systems in the operation of flaps, doors, and landing wheels. Silicone oils also can be used in fine instruments, in watches and clocks, and as a dielectric fluid in capacitors and transformers.

LETTERS

To the Editor:

I have been looking at the pictures in "Teaching technique through cartoons" in the October issue of the JOURNAL OF CHEMICAL EDUCATION. I think the idea is good, but I am annoyed by a statement in the last pair of cartoons. I will grant that the drainage procedure must be standardized in order to obtain a uniform volume. I assert that the drainage procedure should be the same as the procedure used by the man who calibrated the pipet.

For a great many years (since 1908 at least) the U. S. Bureau of Standards has prescribed that transfer pipets are to be used without any drainage period for afterflow. At least the better grades of pipets on the market are calibrated for use as prescribed by the Bureau of Standards. Consequently when students are taught to drain pipets for 30 seconds, they are being taught to introduce an error into each measurement. This is a very common error. It is found in many textbooks, and this is a good time to focus attention upon it.

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To the Editor:

The title of a recent article in THIS JOURNAL [**22,** 554 (1945)], "Can elementary chemistry teaching be logical," certainly was captivating to one who considers chemistry and science in general as a medium of education. The answer that came immediately to mind was another question, "Can *any* teacher afford to be illogical!" Certainly the primary purpose of any education, whatever its medium, is to develop thinkers. Without the ability to think clearly and logically, the mass of scientific data one may possess amounts to merely the scattered parts of a jigsaw puzzle, hopelessly jumbled without hope of bringing from their confusion one clear beautiful picture. Such has not been the history of science. The method of learning by experiment does not mean to try anything and see if it works, but rather try that which has a good chance of success because it is the result of hours and days and nights of sound logical reasoning.

Now, if we take the young mind, and by that I mean the mind we find in high school and early college days, logical thought is not going to be developed by "learning Truth from Experiment only, giving no further credence to argument from Authority." Surely a more efficient method is for the student first to see and understand the clear thought and logical reasoning of one who has given us real chemical knowledge and the worth-while results they have brought. Then follows a sincere appreciation of the value of such a process, a desire to imitate such a process, and finally will come the imitation itself. The teacher who leads a student in great detail through such a process as worked out by our great scientists, using as much demonstration as possible, points out the true working of the scientific method in a great mind and is not guilty of a violation of the scientific method. He is not being illogical.

Frequently the young student is not a skilled worker in the laboratory even in the simple experiments of beginning chemistry. Not all of a class will convincingly verify the law of definite proportions. More often today the student is incapable of drawing the correct conclusions from his work tolerably well done. Should a slavish adherence to a method which demands that the student "learn Truth from Experiment only, giving no credence to the argument from Authority" leave him in his false conclusions or keep him at the same work until he does arrive at the correct conclusion? Or may the authority of the teacher give him the correct conclusions always with the understanding that inexperience has caused him to err, and the conclusion as given is the correct result of the scientific method as worked out by experts? Adherence to the scientific method does not demand that the student accept only what he himself actually has seen in the laboratory, but it permits him to accept on the authority of his teacher what others have done and what he might do either now or at a later date. Neither is the teacher who expects this of his students illogical.

The very beginning of chemistry affords the teacher an excellent opportunity to demonstrate the beauty and value of the scientific method as he unfolds the eminently efficient reasoning process which led to the atomic theory, even if the student cannot work out all the details in the laboratory. He can start with a chemical reaction common in everyday experience, namely burning. He and the students can observe the changes which take place. Now comes the reasoning to explain these changes. The choice can be narrowed down with the aid of the students to three, maybe more, possible explanations: namely, something is gained, something is lost, or the change has taken place without either gain or loss. The way to answer the question properly is by further observation, by actually weighing the substance before and after to find out. The work of Lavoisier can be introduced and appropriate experiments done. The second and "obvious" choice was the answer of the ages. The true answer is that something has been gained. Here the teacher can point out that it is dangerous to draw "obvious" conclusions when experiments, properly done, will give certain answers. He can bring out the dearth of scientific knowledge before this seemingly innocent discovery and the rapid strides made after it had been established as a firm foundation upon which to build. The student will understand that he cannot expect to arrive at true conclusions while arguing from false suppositions. The next step is quantitative and consists in determining the amount a substance in-

(*Continued on page 104*)

CHEMICAL KNOWLEDGE IN THE NEW TESTAMENT

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IN HISTORIES of chemistry very little space is devoted to the bearing of Christianity and the New Testament upon chemistry. The present study was undertaken in order to expand the somewhat cursory accounts available in the standard texts.

As in the case of the Old Testament, we find but little chemical information in the New Testament. While the latter is void of sound theoretical speculation, it contains some practical information dealing with the sources and uses of metallic and nonmetallic substances. Reference is made also to a limited number of simple chemical processes. The New Testament, perhaps because it is inspired by the idea of the renunciation of the material world, contains even less chemical information than is found in the Old Testament.[1] What knowledge of science the early Christians did possess was their heritage from the Hebrews, who in turn had merely borrowed the information from the Egyptians, Babylonians, and Phoenicians.

Palestine and Syria were influenced by Egyptian culture as early as 2000 B.C. Imports from Egypt and Babylonia included red and blue woolen shawls, silver and gold vessels, precious stones, and furniture fashioned of ebony and ivory. Amulets, such as the cross of life, the sphinx, and the solar disc with wings, were also imported from Egypt. Archaeological research conducted in Palestine indicates a much lower state of civilization of the early Israelites than that of the contemporary Phoenicians, Egyptians, or Babylonians.[2] Greek philosophy also influenced the speculative thoughts of the early Christians.

A clear understanding of the chemical insight contained in the New Testament therefore demands the study of the theoretical and practical accomplishments of the more ancient civilizations.

THE METALS

While the metals mentioned in the New Testament are gold, silver, copper, and iron, evidence exists that lead as well as bronze and brass were known even to the inhabitants of Philistine Gezer. The Hebrews did not practice mining or metallurgy, but they were probably acquainted with the processes commonly used in Lebanon. Whereas Palestine is poor in minerals, copper was presumably found in Palestine, Syria, and Lebanon. The existence of iron mines in Lebanon is also alluded to by some authors.[3]

The chief producers of gold were Sheba, Ophir, Uphaz, Parvaim, and Havilah. Palestine itself had no gold.[4] Nevertheless, the Jews, by the time of the early Christians, were expert gold workers. Beating into leaves, drawing into wire, hammering, and casting were common ways of working gold since the earliest Semitic Period. Even Moses was familiar with the art of working gold since he "was learned in all the wisdom of the Egyptians" [(**Acts** 7:22).[5] The numbering of the verses follows that used in the King James' version of the Bible.] Pliny describes an amalgamation process for the extraction of gold and silver which in some respects resembles the modern methods.[6] According to Napier, the ancients used three methods for the purification of gold. In one method the impure metal was fused and then exposed to a current of air. By another procedure the molten alloy was treated with niter. In the third process the impure gold was mixed with lead and the whole exposed to fusion by heating in an earthen vessel, the fusion being accompanied by the blowing with bellows. The latter method was claimed to be superior to the other processes.[7] A more detailed account of the refining of gold as practiced by the ancients is outlined by Berthélot. According to him, the contaminated gold was heated in an earthen vase with twice its weight of salt and three times its weight of a product of the slow oxidation of pyrites; the process of heating was repeated with two parts by weight of salt and one part by weight of schist.[8] With reference to the purification of gold, Partington makes the following statement: "So far as is known, all ancient processes for the separation of gold from silver or other metals depended on a dry method of heating with salt, misy (impure iron sulfate), and other materials, still used in the 18th century."[9]

Archaeological researches conducted by Petrie disclose evidence that gold was used abundantly as early as 1190 B.C. It was numbered among the luxuries which comprised the merchandise of Babylon (**Revelation** 1:12). Its preciousness is further indicated by the fact that it was included among the gifts from the Wise Men of the East to Jesus (**Matthew** 2:11). Gold was used for articles of apparel. Wealthy women bedecked themselves with gold (**Revelation** 17:4) and wore golden girdles (**Revelation** 1:13). Eight gateways of the temple were supplied with

[1] WEEKS, M. E., "An exhibit of chemical substances mentioned in the Bible," J. CHEM. EDUC., **20**, 63–76 (1943); ISSERROW, S., AND H. ZAHND, "Chemical knowledge in the Old Testament," *ibid.*, **20**, 327–35 (1943).

[2] PARTINGTON, J. R., "Origins and Development of Applied Chemistry," Longmans, Green & Company, London, **1935**, pp. 467–71.

[3] PARTINGTON, *ibid.*, pp. 481–2.

[4] M'CLINTOCK, D. D., AND J. STRONG, "Cyclopaedia of Biblical, Theological and Ecclesiastical Literature," Harper and Brothers, New York, **1869–81**, Vol. 3, 916–7.

[5] WEEKS, *op. cit.*, **20**, 64 (1943).

[6] NAPIER, J., "The Ancient Workers and Artificers in Metal," Griffin Company, London and Glasgow, **1858**, p. 18.

[7] *Ibid.*, p. 20.

[8] BERTHÉLOT, M. P. E., "Introduction à l'étude de la Chemie des anciens et du moyin âge," Paris, **1889**, p. 14.

[9] PARTINGTON, *op. cit.*, p. 486.

folding doors overlaid with gold and silver (**Acts** 3:2).[10] Inside, among the furnishings of the temple, were to be found golden candlesticks (**Revelation** 1:12), a golden censer, and a golden altar (**Revelation** 8:3). The metal was commonly used for jewelry, especially for the manufacture of rings (**James** 2:2). These rings, which were considered as an indispensable part of the fashionable attire, were sometimes made of iron inlaid with gold. The rings of the early Christians were adorned with symbols of faith.[11] Vials (**Revelation** 15:7) and cups (**Revelation** 17:4) made of gold are also mentioned in the New Testament. The quotation "a golden rud to measure the city" indicates yet another use for this element (**Revelation** 21:15). The pagan Greeks used gold to make idols, the commonest of which were made of wood decorated with gold, while others were cast in gold.[12] For these idols of gold the Christians had nothing but contempt.

While spiritual wealth was considered far superior to treasures of gold (**Matthew** 10:9; **James** 5:3; **I Peter** 1:7, 18–19; **Acts** 17–29), the material value of the latter was fully appreciated (**Revelation** 3:18, 4:4; **I Corinthians** 3:12).[13]

Silver was plentiful in Palestine during the reign of Solomon (about 950 B.C.). At this time silver came from Arabia and from Tharshish. The latter country was perhaps Spain or possibly Assur. The possibility exists that some silver may have been found in Palestine. Silver was probably refined by means of heating and its cupellation in the presence of lead was also practiced.[14]

The chief use of silver was for money (**Luke** 15:8; **John** 2: 15). The "denarius," a silver coin issued by the Roman Imperial mint, bore on one side the head of the Emperor (or some member of the Imperial family) in conjunction with superscriptions[15] (**Matthew** 22: 20; **Mark** 12:16; **Luke** 20:24). These coins were used for the paying of tribute. Other coins in common use were the "farthing" (**Matthew** 5: 26; **Mark** 12:42; **Matthew** 10:29; **Luke** 12: 6) and the "stater"[16] (**Matthew** 17:27; 26:15; 27:3–5), the latter being a Phoenician standard. Silver was also used for the making of idols[17] (**Revelation** 9:20) and shrines. These silver shrines were small models of the temple of Diana, containing an image of the goddess. Pilgrims purchased these replicas on their way to the temple.[18] Demetrius, a silversmith, made such shrines (**Acts** 19: 24). Paul despised these idols and thus aroused the anger of Demetrius and his fellow craftsmen (**Acts** 19: 26).

Copper evidently was known and used before the flood. Petrie disclosed the existence of copper rings and of copper beads of the years 2000 B.C. and 1180 B.C., respectively. While the Hebrews probably never smelted the metal themselves, they were acquainted with the metallurgical processes used by the Egyptian metal workers. The Sinai peninsula was the earliest source of Egyptian copper.[19] Since copper is found in Lebanon, Palestine, and Syria, the assumption that King Solomon opened copper mines in Lebanon is most likely correct. According to Partington, the large copper pieces used for the construction of the temple were made under the supervision of Phoenician artisans.[20] While most coppersmiths settled in Alexandria,[21] Alexander, the coppersmith who opposed Paul, lived in Ephesus[22] (**II Timothy** 4:14). Copper, too, was commonly used for coinage. The widow's mites were probably small copper coins[23] (**Luke** 21: 2; **Mark** 12:43). According to Napier, copper was not used in the pure state as it was difficult to toughen, tarnished easily, and formed toxic compounds on its surface. Because of the latter property it was not used for the manufacture of kitchen utensils.[24]

Inasmuch as the Hebrew as well as the classic Greek use one word for copper, bronze, or brass, the translations become ambiguous. "Brass" as used in the Authorized Version, probably often signifies copper or bronze; "brazen" objects, on the other hand, were most likely composed of bronze. The "fine brass" of the New Testament, according to M'Clintock and Strong, refers to still another alloy composed of gold and silver.[25]

Of the copper alloys, bronze came into use no later than about 2000 B.C. According to Partington, this alloy was particularly abundant from the earliest "Amorite" period to 1350 B.C. Cooking pots, knives, arrow-heads, mirrors, and axes are but a few of the objects which were composed of bronze. Early bronzes varied considerably in composition and thus indicated a lack of skill in metallurgical procedure.[26] "Brazen" (bronze) vessels of all types were in common use (**Mark** 7:4). Pans, shovels, arms, decorative designs of the Tabernacle, fetters, bows, and the bronze sea cast for Solomon were fashioned from this alloy. Jesus spoke in the treasury where the contribution for the temple were kept in thirteen "brazen"

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[10] DELITZSCH, F., "Jewish Artisan Life in the Time of Jesus," translated from 3rd revised ed. by PICK, Funk and Wagnalls, New York, 1883, p. 19.

[11] VINCENT, M. R., "Word Studies in the New Testament," Charles Scribner's Sons, New York, 1890, "James," Vol. 1, p. 738.

[12] CHEYNE, T. K., AND J. S. BLACK, "Encyclopaedia Biblica," A. and C. Black, London, 1899, Vol. 2, p. 2151; Revelation 9: 20.

[13] M'CLINTOCK AND STRONG, *op. cit.*, Vol. 3, pp. 916–7.

[14] PARTINGTON, *op. cit.*, p. 487.

[15] CHEYNE AND BLACK, *op. cit.*, Vol. 3, pp. 3646–8.

[16] CHEYNE AND BLACK, *op. cit.*, Vol. 4, p. 4786.

[17] CHEYNE AND BLACK, *op. cit.*, Vol. 2, p. 2151.

[18] VINCENT, *op. cit.*, "Acts," Vol. 1, p. 554; WHEELER, J. T., "An Analysis and Summary of New Testament History Including the Four Gospels Harmonized, the Acts, and Analysis of the Epistles and the Book of Revelations: The Critical History' Geography, etc.; with Copious Notes, Historical, Geographical and Antiquarian," Arthur Hall, Virtue and Company, London, 1853, "Acts of the Apostles" p. 91.

[19] DAVIS, W. C. E., "Story of Copper," The Century Company, New York, 1924, p. 19.

[20] PARTINGTON, *op. cit.*, p. 489.

[21] DELITZSCH, *op. cit.*, p. 41.

[22] *Ibid.*, p. 9.

[23] WEEKS, *op. cit.*, p. 65.

[24] NAPIER, *op. cit.*, pp. 62–6.

[25] M'CLINTOCK AND STRONG, *op. cit.*, Vol. 1, p. 878.

[26] PARTINGTON, *op. cit.*, pp. 474–5.

vessels[27] (**John** 8:20). Moses made a "brazen" serpent which was supposed to protect against bites of venomous snakes and which Christ later declared to be a symbol of Himself crucified.[28] The "beautiful gate" mentioned in the New Testament probably derived its name from the bas-relief lily-work in Corinthian "brass" with which some of the folding doors of the temple were decorated[29] (**Acts** 3:10). "Brass" was often highly polished (**Revelation** 1:15). Helmets, apparently manufactured of bronze, were worn by distinguished men while engaged in battle.[30] To the Christian, a helmet was the symbol for salvation (**Ephesians** 6:17; **I Thessalonians** 5:8).

The alloy brass was known early in the Holy Land (1400–1000 B.C.).[31] The brass-makers were not familiar with zinc in the pure state; instead, they used the ore calamine, a hydrated zinc silicate, to form the brass called aurichalcum in early Roman writings.[32] The brass was most likely used for the manufacture of bells and cymbals (for reference see footnote 31).

Studies undertaken by Petrie show the existence of iron works in Palestine at an early date (1300 B.C.). He expresses also the view that the early Israelites were acquainted with steel. Objects manufactured of iron before the time of David include an iron ring (1180 B.C.), tools (1170 B.C.), and a broken steel dagger (1350 B.C.). At the time of David (1000 B.C.) tools and weapons were fashioned of iron. It appears that the working of iron did not originate in Palestine. While the Bible gives no clue as to the origin of the use of iron, it is known that the Philistines were well acquainted with the art of working iron. The Philistines probably acquired the skill from the Hittites. In the time of Solomon (960 B.C.) the Phoenicians were noteworthy for their skill in metal working. By the time of Amos (760 B.C) iron was in general use by the ancient Hebrews. Swords, chains, axheads, chariots, and other objects too numerous to mention were fashioned of iron at an early date. Due to the bias against the employment of iron for religious ceremonies, this element was not used in the construction of the Tabernacle.[33]

Up to the time of 1000 B.C. much of the iron used was of foreign origin, most likely from the iron works situated in Asia Minor. Iron ore is abundant in Palestine and Syria. Deposits of the metal were found in Judea and Lebanon.[34] Iron furnaces dating as far back as 1200 B.C. were disclosed by Petrie. Wood, instead of coal, was used as a source of heat for the smelting process. Josephus mentions the "Iron Mountain" which is one of the peaks bounding the valley of the Jordan north of the Dead Sea.[35] The "Rose Mines," which were worked by Ibrahim Pasha from 1835–9, are among the iron mines found in the region east of the Jordan.[36] Thus it is quite possible that iron was obtained not only from ores found on the surface but also by means of mining processes. According to Napier, there is no evidence that the ancients were acquainted with cast iron; however, they did possess malleable iron and steel.[37] Products composed of this metal and mentioned in the New Testament are gates (**Acts** 12:10), fetters and chains (**Mark** 5:4), breastplates (**Revelation** 9:9; **I Thessalonians** 5:8), helmets (**I Thessalonians** 5:8), nails (**John** 20:25), and axes (**Luke** 3:9; **Matthew** 3:10; **Revelation** 20:4). Paul used the term breastplate as a symbol for the righteousness of the Christian warrior. The breastplate was either a corselet of scale armor or a cuirass of broad plates across the chest and long flexible bands of steel across the shoulders (**Ephesians** 6:14). Iron is used symbolically to represent firmness (**Revelation** 2:27).

The terms amber and electrum have not been clearly defined. Amber (chasmil) as referred to by some writers indicates an alloy composed of several metals. According to M'Clintock and Strong, the fine brass mentioned in the New Testament (**Revelation** 1:15) refers to this type of amber.[38] Electrum probably signifies an alloy of the composition of gold and silver.[39, 40] This alloy served for the making of coins in Asia Minor.

Lead, which was an article of commerce at Tyre, was used for the preparation of various alloys. Thus Roman monetary bronze at times contained some lead.[41, 42] According to Partington, this metal may have had its origin in the mines of Gebel Rusâs (near the Red Sea).

The chief use of tin was as a constituent of the alloy known as bronze. The element was brought to Tyre and other centers of commerce by Phoenician merchants from Spain, to which country it came from Britain (Cornwall).

PRECIOUS STONES

From the geological character of the mountains in Syria it can be ascertained that they contain topaz,

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[27] WHEELER, *op. cit.*, "The Gospels," pp. 105–6.
[28] KITTO, J., "Palestine, the Biblical History of the Holy Land," Charles Knight and Company, London, **1841**, p. 318.
[29] WHEELER, *op. cit.*, "Acts of the Apostles," p. 20; DELITZSCH, *op. cit.*, p. 19.
[30] CHEYNE AND BLACK, *op. cit.*, Vol. 2, pp. 2013–4.
[31] PARTINGTON, *op. cit.*, pp. 83, 475–6, 490.
[32] DAVIS, *op. cit.*, pp. 14–5.
[33] PARTINGTON, *op. cit.*, pp. 476, 491–3.
[34] HASTINGS J., "A Dictionary of the Bible," Charles Scribner's Sons, New York, **1898**, "Mining and metals," Vol. 3, pp. 374–5.
[35] KITTO, J., "Palestine, The Physical Geography and Natural History of the Holy Land," Charles Knight and Company, London, **1841**, p. lxxi.
[36] DELITZSCH, *op. cit.*, p. 26.
[37] NAPIER, *op. cit.*, p. 137.
[38] M'CLINTOCK AND STRONG, *op. cit.*, Vol. 1, p. 191.
[39] FALLOWS, S., "Popular and Critical Bible Encyclopaedia and Scriptural Dictionary," Howard-Severance Company, Chicago, **1903**, Vol. 1, pp. 394–5.
[40] The terms amber and electrum are often used interchangeably by the ancients to designate one of the following substances: (1) an alloy composed of gold and silver; (2) amber; (3) glass; (4) shellac.
[41] FALLOWS, *op. cit.*, p. 244.
[42] BERTHÉLOT, *op. cit.*, p. 55.

emerald, chrysoberyl, several varieties of rock crystal, and the finer grades of jasper.[43] The precious stones enumerated in the Book of Revelation are jasper (**Revelation** 4:3; 21:11, 18, 19), sardius (**Revelation** 4:3; 21:20), emerald (**Revelation** 4:3; 21:19), sapphire, chalcedony, sardonyx, chrysolite, beryl, topaz, chrysoprasus, jacinth, and amethyst (**Revelation** 21:19, 20). [44]

It appears that most of the information gathered on gems named in the New Testament is derived from the knowledge as disclosed by Pliny. But since the identification of precious stones by the classical writers is far from lucid, the establishment of the identity of these gems remains uncertain. The modern terminology for the precious stones mentioned in the Book Revelation does not correspond in every case to the name found in the authorized version of the English Bible.[44]

The Temple in Jerusalem was decorated with diverse precious stones (**Luke** 21:5). The references to crystal found in the Book of Revelation designate probably rock crystal. Theophrastus classifies crystal among the pellucid stones used for engraved seals (**Revelation** 4:6; 21:11; 22:1).[45] Jasper, as the word appears in the Authorized Version of the New Testament, probably does not indicate the mineral we know as jasper. Jasper is not a translucent stone, yet in **Revelation** 21:11 the stone is described as being "clear as crystal." This suggests its identification as a superior variety of jade or nephrite. Jasper, as we know it, is an opaque quartz (a variety of chalcedony), of red, yellow, or putty color. Jade, on the other hand, is translucent and has been used for jewelry, cups, bells, and priceless bowls. Since diamonds were probably known to the earlier Jews, jasper has also been assumed by some to be identical with diamond.

The name sapphire very probably indicated the modern lapis lazuli. The latter stone has been mined for the longest time in Afghanistan. The best specimens are golden due to the presence of iron pyrites.

Chalcedony probably refers figuratively to a green variety of chalcedony found at Chalcedon. It is a cryptocrystalline quartz called carnelian, onyx, sardonyx, or sard, depending on its staining. It has been used by gem engravers since antiquity. Pliny uses the name "calchedoni smaragdi" for an inferior kind of emerald. A mountain located in Chalcedon apparently was the source for this variety of precious stone.[46]

The word emerald has been correctly rendered in the New Testament. It is composed of silicate of aluminum and beryllium and is extremely costly when it is large, flawless, and brilliant. A possible source for this gem was certain mines at Zabara on the borders of Egypt. At present the chief source for the true emerald is Colombia. The ancients attributed great magic virtues to the emerald. Improving vision, coloring water green, easing the pain of childbirth, and driving away evil spirits were some of the magic powers ascribed to this precious stone. The green color of this gem is due to the presence of a chromium compound.[47]

The sardonyx of antiquity is probably identical with the stone known at present by this name. It is an onyx with the addition of a third layer of sard.

The sardius of the New Testament is identical with the sard, a variety of carnelian of deep tinge. It apparently was extensively used for the manufacture of intaglios and signets.

The gem referred to as chrysolite in **Revelation** is now called topaz. Topaz, as we understand the term, may be blue, green, pink, brown, yellow, or even white. When heated, the yellow variety changes to pink topaz.

It is most likely, but not certain, that the beryl of the ancients is identical with modern beryl. Beryl as a mineral species includes the common beryl, the aquamarine, and the emerald. While the beryl is related to the emerald, it cannot compare to it in value. It is interesting to note that the similarity between the beryl and the emerald was pointed out by Pliny. Gem-engraving in beryl was practiced by the ancient Greeks and Romans. The beryl may be green, light blue, pink, yellow, or white in color.

The topaz of the ancients is identical with the chrysolite of modern times. Chrysolite, also called olivine or peridot, is an olive-green magnesium iron silicate.

The chrysoprasus is probably identical with the apple-green type of chalcedonic quartz now named chrysiprase.

The term jacinth as found in the **Revelations** appears to indicate the modern sapphire. The sapphire, as identified by modern man, is a transparent variety of aluminum oxide or corundum. According to Cheyne and Black, the hyacinthus of the ancients was probably also identical with our sapphire.[48] The most valuable sapphires are "velvet" or "corn flower" blues.

The amethyst is identical with the stone known to-

[43] RUSSELL, M., "Palestine or the Holy Land from the Earliest to the Present Time," Harper and Brothers, New York, 1836, p. 308.

[44] According to HURBLUT, J. G., AND A. J. P. MCCLURE, Editors, "The International Teachers' Handy Bible Encyclopedia and Concordance," Garden City Publishing Company, New York, 1940, p. 272, the following comparison may be made:

Authorized Version	*Modern Names*
Jasper	Jade
Sapphire	Lapis Lazuli
Chalcedony	Chalcedony
Emerald	Emerald
Sardonyx	Sardonyx
Sardius	Sard
Chrysolite	Topaz
Beryl	Beryl
Topaz	Chrysolite
Chrysoprasus	Chrysiprase
Jacinth	Sapphire
Amethyst	Ameythist

[45] CHEYNE AND BLACK, *op. cit.*, Vol. 2, p. 964.

[46] CHEYNE AND BLACK, *op. cit.*, Vol. 1, pp. 719–20.

[47] CHEYNE AND BLACK, Vol. 2, pp. 1287–8.

[48] CHEYNE AND BLACK, *op. cit.*, Vol. 1, p. 2305.

day by this name. It is a form of quartz, silicon dioxide, or rock crystal possessing a clear bluish-violet or purple color due to the presence of an oxide of iron or manganese. Its Greek name implies the belief that its wearer could drink wine freely and yet retain his normal senses.[49] Theophrastus was the earliest Greek writer to allude to this magic property; the wine color of the amethyst, it was argued, resists the intoxicating effects of the wine. This is clearly a case of sympathetic magic.[50] In this connection it is interesting to note that many wine glasses were made of amethyst in ancient Rome.

While the later Jews were acquainted with the imitation of gems by means of colored glass, neither the Old Testament nor the New Testament refers to this art.[51]

Pearls are mentioned several times in the New Testament (**Matthew** 7:6; 13:45, 46; **I Timothy** 2:9; **Revelation** 17:4; 18:12; 21:21). Pearls are produced within the shell of numerous tropical mollusks, particularly by the species Meleagrina or Margaritifera. They are found in the Persian Gulf, the Red Sea, and elsewhere.

COMMERCIAL PRODUCTS

Because sulfur burns so easily, the old popular name of this element is "brimstone" or "brennestone"—that is, "burnstone." Brimstone is frequently referred to in connection with divine judgment (**Luke** 17:29; **Revelation** 9:17; 14:10; 19:20; 20:10; 21:8).[52]

While the authors of the New Testament do not indicate any practical use to which sulfur was put by the Jews, Pliny claims that the ancients used the element for the process of lamp fumigation and for the cleaning of wool. There is also evidence available that sulfur was used for the preparation of certain medical remedies and in connection with ceremonies dealing with religious purification. Perhaps the Hebrews, as well as the Greeks and Romans, connected the ozonic smell formed during lightning discharges with the presence of sulfur. In such wise the allusion to the overthrow of Sodom and Gomorrah, caused by a rain of fire and brimstone from heaven, may be explained (**Luke** 17:29). The fact that the Hebrews were acquainted with the volcanic phenomenon known as "solfatara" and with "firewells" forms the basis for another interpretation of the account of the destruction of these cities.[53] Sulfur was found in Palestine on the Hill of Tiberias and its immediate neighborhood, along the shores of the Dead Sea, and in the warm springs of the volcanic valley of the Jordan.[54, 55]

Salt was widely used for sacrificial purposes (**Mark** 9:49–50). Figuratively speaking, salt is used as a symbol for faithfulness, purity, and lastingness (**Colossians** 4:6). This idea is also embodied in the words of Jesus to his disciples: "Ye are the salt of the earth" (**Matthew** 5:13). Speech seasoned with salt indicates moderate, discrete conversation (**Colossians** 4:6). The Israelites believed that exposure to air destroyed the efficacy of the antiseptic property of salt (**Matthew** 5:13) and rendered it "saltless" (**Mark** 9:50). The more inferior grades of salt were used as soil fertilizers or were spread on the dunghill (**Matthew** 5:13; **Luke** 14:35) to speed the decomposition of the dung.[56]

Salt is found under various conditions in numerous localities in Palestine. Great quantities of salt are washed up along the shores of the Dead Sea. Rock salt is found in large amounts at the southern end of this body of water. The high concentration of salt found in the latter is believed to originate in the strata of rock within its basin. This theory is supported by the fact that a hill near its shore is made up partly of salt and by the evidence that large crystal formations composed of salt are found suspended from cliffs in many places. Strabo claims that towns and villages made entirely of salt were located to the south of the Dead Sea.[57]

The ancient Jews became acquainted with the use of glass at an early date (1400–1000 B.C.).[58] The oldest examples of the art of glass making came to Palestine from countries situated around the Nile, the Tigris, and the Euphrates. In Egypt and Babylonia glass was deemed most precious, a fit offering to the Gods.[59] Glass was made in Syria and Palestine as early as the Roman period and by the time of the early Christians was of good quality, abundant, and cheap. Skilled glass workers were numbered among the residents of Alexandria as well as among the Romans. The early artisans were familiar with the manufacture of colorless as well as colored glass. It has been established that during the later Roman Empire the Phoenician glass works in Tyre were operated by Jews.[60]

The transparency of glass and its sparkling appearance were highly priced by the early Christians (**Revelation** 4:6; 15:2; 21:11, 18, 21; 22:1). Most authorities believe that the references to mirrors in the Authorized Version of the New Testament (**I Corinthians** 13:12; **II Corinthians** 3:18; **James** 1:23) indicated metal discs with ornamental handles instead of looking glasses. These polished metal mirrors were fashionable at that time in Greek society.[61]

Clay was used in Palestine mainly for the manufacture of bricks and kitchen utensils (pottery), the construction of ceilings and floors, and the fabrication

[49] CHEYNE AND BLACK, *op. cit.*, Vol. 1, p. 138.
[50] CHEYNE AND BLACK, Vol. 1, p. 138.
[51] PARTINGTON, *op. cit.*, p. 507.
[52] CHEYNE AND BLACK, *op. cit.*, Vol. 1, p. 611.
[53] CHEYNE AND BLACK, *op. cit.*, Vol. 1, p. 611.
[54] RUSSELL, *op. cit.*, pp. 305–6.
[55] VINCENT, *op. cit.*, "James," Vol. 1, p. 752.
[56] M'CLINTOCK AND STRONG, *op. cit.*, Vol. 9, pp. 259–60.
[57] KITTO, J., "Palestine, The Physical Geography and Natural History of the Holy Land," Charles Knight and Company, London, 1841, p. lxx.
[58] PARTINGTON, *op. cit.*, p. 499.
[59] CHEYNE AND BLACK, *op. cit.*, Vol. 2, pp. 1737–8.
[60] PARTINGTON, *op. cit.*, p. 500.
[61] CHEYNE AND BLACK, *op. cit.*, Vol. 3, p. 3153.

of tablets to be used for the inscription of important documents. Clay instead of wax was used for sealing.[62] The belief that kilns existed which were used for the manufacture of large storage vessels for water and wine is supported by considerable evidence.[63] The Israelites learned brick-making from the Egyptians and brick kilns were used at an early date by the Jews. Pottery making and the use of the potter's wheel was also introduced by way of Egypt. Various forms of clay vessels are mentioned in the New Testament.[64] Thus we find reference to a large vessel for carrying water (**John** 4:28), to a drinking cup (**Mark** 7:4; 14:13; **Luke** 22:10), and to potsherds (earthen vessels of undefined shape) used to preserve buried treasure (**II Corinthians** 4:7).[65] Perrot, in his "History of Art in Sardinia, Judaea, Syria, and Asia Minor," gives an account of vases shaped like pine cones which were used for the importation of mercury. These vessels apparently were of foreign origin.[66] Due to the fragility, pottery was not considered very valuable and was therefore put to menial use (**Revelation** 2:27; **II Timothy** 2:20).[67] Yet Jesus used this same humble clay to anoint the eyes of a blind man in order to restore his sight (**John** 9:6).

The use of stone for practical purposes is also indicated in the New Testament. Limestone, basalt, sandstone, various kinds of marble, flint (a translucent brown or smoky gray to black form of chalcedonic quartz), serpentine rock, gypsum, Egyptian "alabaster," and other stones were used by the Jews for masonry and other common purposes.[68, 69] The body of the departed was safeguarded by closing the entrance to the sepulchre with a large stone (**Mark** 15:46). The tombs of the wealthy were hewn in stone (**Luke** 23:53)[70] and the ministration of the death was engraven in stone (**II Corinthians** 3:7). Waterpots made of stone are alluded to in the New Testament (**John** 2:6). Vases made to hold unguents were frequently made of Egyptian alabaster, the name being derived from a city in Egypt, Alabastra, near which were located quarries of this variety of stone. Alabaster, as we understand the term, is a form of gypsum, white or delicately tinted, frequently translucent, and used for the manufacture of ornamental objects and statuary. This is not to be confused with the alabaster of ancient times which was a fine grade of stalagmitic carbonate of lime and was also used for ornaments and vases. According to Partington, alabaster as referred to in the New Testament is a variety of calcite (calcium carbonate, crystallizing in the rhombohedral division of the hexagonal system).[71] The "alabaster" cruse (**Matthew** 26:7; **Mark** 14:3; **Luke** 7:37) mentioned in the story of Mary of Bethany was a cruet with a cylindrical top and made of calcite ("Egyptian alabaster," "Oriental alabaster"). Pliny compares these vessels poetically with a closed rosebud and states that ointments are best preserved in them.[72] "Brake" in Mark does not indicate the breaking of the seal or the neck of the cruse but refers to the shattering of the vessel and thus prevents its profanation by any future menial use.[73] Marble was included among the fabulous merchandise of Babylon (**Revelation** 18:12).

On Mt. Carmel and near Bethlehem are found certain products of processes of crystallization called "Elijah's melons" and the "Virgin Mary's peas." Silicious accretions shaped like little loaves of bread became legendary as the petrified fruits of the cities of the plain. It is perhaps the resemblance of these silicious accretions to little loaves of bread that prompted Christ to say, "Or what man is there of you, who, if his son shall ask him for bread, will give him a stone" (**Matthew** 7:9).[74]

Several symbolic references are made to stone or rock. Simon, the son of Jona, is called Cephas, which may be interpreted as "a stone" (**John** 1:42). A white stone is mentioned by Jesus in the message to the churches (**Revelation** 2:17). The rejected stone alluded to by Christ is probably a symbol of Himself (**Matthew** 21:42; **Luke** 20:17).

The term "pitch," as used in the Authorized Version of the Old Testament, signifies that the ancient Israelites were familiar with the bitumen or asphalt found in the valley of the Jordan and in or close to the Dead Sea. The Jews used this material for the caulking of wood, the preparation of medicinals, and as a mortar or cement for building.

The making of bread was practiced by the Egyptians at an early date. They made little rolls from white flour which were similar in shape to our muffins. Public bakeries in ancient Greece and Rome signify the widespread practice of bread making. The flour used by the Jews for the baking of bread was prepared by grinding wheat, corn, barley, or rye in stone mortars. The product was then passed through a sieve. The best bread was apparently made from wheat flour. "Fine flour" is specified as one of the articles of merchandise of fallen Babylon (**Revelation** 18:13). While baking at home was done by women, public bakeries employed men for this purpose. The bakeries in Palestine were restricted to specified districts in the towns. The leaven used for the preparation of bread was a piece of entirely fermented dough which was mixed with the flour (**Matthew** 13:33; **Luke** 13:21).

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[62] CHEYNE AND BLACK., Vol. 1, p. 836.
[63] PERROT, G., AND C. CHIPIEZ, "History of Art in Sardinia, Judaea, Syria and Asia Minor," Armstrong and Son, New York, 1890, Vol. 1, p. 352.
[64] CHEYNE AND BLACK, *op. cit.*, Vol. 3, pp. 3815–9.
[65] CHEYNE AND BLACK, *ibid.*, Vol. 3, pp. 3815–9.
[66] PERROT AND CHIPIEZ, *op. cit.*, Vol. 1, p. 357.
[67] CHEYNE AND BLACK, *op. cit.*, Vol. 3, pp. 3815–9.
[68] FALLOWS, *op. cit.*, Vol. 2, p. 1614.
[69] PARTINGTON, *op. cit.*, p. 501.
[70] VINCENT, *op. cit.*, "Matthew," Vol. 1, p. 125.
[71] PARTINGTON, *op. cit.*, p. 501.
[72] VINCENT, *op. cit.*, "Matthew," Vol. 1, p. 136.
[73] CHEYNE AND BLACK, *op. cit.* Vol. 1, p. 108.
[74] VINCENT, *op. cit.*, "Mathew," Vol. 1, p. 27.

Christ used the word "leaven" in a figurative sense to denote the growth of the kingdom within the mass of humanity (**Matthew** 13:33). Fermentation of bread was associated with the progress of spiritual corruption and the disciples were cautioned to guard against the leaven of the Pharisees (**Matthew** 16:6; **Mark** 8:15; **Luke** 12:1), of the Sadducees (**Matthew** 16:6), and of Herod (**Mark** 8:15). "A little leaven leaveneth the whole lump" (**I Corinthians** 5:6; **Galatians** 5:9). The true believers are "unleavened" and must continue to live by "unleavened bread of sincerety and truth" (**I Corinthians** 5:7–8).[75]

Among the trees yielding edible products (almond, date, quince, pomegranate, fig, apple, walnut, etc.) and known before or by Roman times, the olive tree is of particular importance. The latter tree is a native of southwestern Asia but was cultivated since remote antiquity in the Holy Land for its fruit. Records indicate that the ancient Israelites found fruit-bearing olive trees in Canaan. The ancient Egyptians also cultivated the olive. Homer refers to it in the "Odyssey" and in the "Iliad." According to Pliny, the Romans became acquainted with the cultivated fruit during the reign of the fifth legendary king of Rome (Tarquinius Priscus, 627 B.C.). Pickled olives, a table delicacy since Roman times, have been recognized among the buried treasures in Pompeii. The ancient inhabitants of Southern Europe used the olive as a symbol of peace and wealth. In Rome, an olive crown characterized the victor in war; and in Greece, an olive spray designated the winner in the Olympic games. Today, as in ancient times, the products derived from the fruit of the tree are of great value. The ancients used the oil as food, for the preparation of medicinals, for lighting, for anointing, and for dressing of goods fashioned from leather. The tree lives to an enormous age and bears fruit to the last.

The references to oil in the Bible refer to olive oil. This oil was often used as a fuel for lamps (**Matthew** 25:4) and for the preparation of unguents, the latter being used for the anointing of corpses (**Matthew** 26:12; **Luke** 23:56; **Mark** 14:3; **John** 19:40). The traveler provided himself with oil for his journey (**Luke** 10:34). From its use for the toilet of the feast it became to the Hebrews "a symbol of joy," therefore the use of the expression "the oil of gladness" (**Hebrews** 1:9).[76] The process of anointing was used for secular as well as sacred purposes. The unguent consisted of olive oil with or without added aromatic spices. Since anointing was a necessary part of the complete toilet, its omission indicated mourning. The parts of the body most usually anointed were the head and face; anointing of the feet was considered a special luxury (**Luke** 7:46). Oil and wine were used for the treatment of wounds (**Mark** 6:13; **Luke** 10:34). Hippocrates indicates the following treatment for ulcers: "Bind with soft wool and sprinkle with wine and oil.[77] The function of anointing during sacred rites is not clearly indicated, but it may possibly be connected with the magical and religious properties which were associated with the oil which was used for the anointing of the sick (**Mark** 6:13; **James** 5:14). Metaphorically speaking, the word anointing is associated with the concept of God's spirit flowing out upon man (**Luke** 4:18; **II Corinthians** 1:21; **Acts** 10:38). "The anointing from the holy one" (**I John** 2:20–7) relates to the special knowledge of all things by those who accept the Holy Spirit.[78]

The ancient Hebrews used olive oil (derived from the olive by crushing the latter with stone rollers or stone weights) as a fuel for lamps; in more recent times other oils (fish oil, nut oil, and other varieties) or naphtha have been used for this purpose.[79]

Inks were used by the Chinese and the Egyptians as early as 2500 B.C. The writing fluid used by the ancient Jews was composed of powdered charcoal, lampblack or soot, mixed with gum and water. It retained its deep black color indefinitely but was easily washed from the surface of the parchment paper with the help of a sponge and water.[80] This ink was much less fluid than the modern variety. Colored inks, such as red, blue, purple, gold, and silver were also used by the ancients.[81] Since carbon ink does not write clearly on parchment paper, the possibility exists that the Israelites were acquainted with iron gall ink. In addition to writing on papyrus paper, the ancient Jews wrote on tablets of stone or wood and also on skins.

The fact that carbon ink is easily removed by washing with water gives point to John's words "Having many things to write unto you, I would not write with paper and ink" (**II John** 1:12; **III John** 1:13). The statement, "Forasmuch as ye are manifestly declared to be the epistle of Christ ministered by us, written not with ink, but with the Spirit of the living God," points to Paul's acquaintance with this writing fluid (**II Corinthians** 3:3).

The preparation and use of leather were long familiar to the Hebrews.[82] Preceding the process of tanning, the hair was removed from the skins by treatment with lime.[83] Tanning, which brought the workman in contact with filth and thereby made him personally offensive, was held in low esteem. This attitude of Hebrew society was due, no doubt, to the fact that the Mosaic law had instilled in the people a strong dislike for the unclean. Since tanning was considered an unclean trade, tanneries could not be erected within the city boundaries.[84]

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[75] CHEYNE AND BLACK, *op. cit.*, Vol. 3, p. 2752.
[76] CHEYNE AND BLACK, *op. cit.*, Vol. 3, pp. 3466–71.
[77] VINCENT, *op. cit.*, "Luke," Vol. 1, p. 356.
[78] CHEYNE AND BLACK, *op. cit.*, Vol. 1, p. 172.
[79] PARTINGTON, *op. cit.*, pp. 511–2.
[80] CHEYNE AND BLACK, *op. cit.*, Vol. 2, p. 2169.
[81] FALLOWS, *op. cit.*, Vol. 1, p. 172.
[82] CHEYNE AND BLACK, *op. cit.*, Vol. 3, p. 2751.
[83] RODWELL, G. F., "The Birth of Chemistry," The Macmillan Company, London, **1874**, p. 50.
[84] DELITZSCH, *op. cit.*, pp. 41–2.

Peter, while residing in Joppa, stayed at the house of a tanner by the name of Simon (**Acts** 9:43; 10:6). Paul, although a Rabbi, was required by custom to learn a trade. "And because he was of the same craft, he abode with them, and wrought: for by their occupation they were tentmakers" (**Acts** 18: 3). It should be noted that Paul really was not a maker of tents but rather was skilled in the manufacture of tentcloth.[85] This cloth, a thick felt-like material used for covering tents, was made from the hair of very shaggy goats.[86]

Other leather articles were girdles (**Matthew** 3:4) and probably purses, wallets, and shoes (**Luke** 10:4). Sackcloth, used as attire during periods of mourning, was made of goat or camel hair similar to that used for tent-making.[87]

[85] DELITZSCH, *op. cit.*, p. 81.

[86] WHEELER, *op. cit.*, "Acts of the Apostles," p. 80.

[87] VINCENT, *op. cit.*, "Luke," Vol. 1, p. 351.

[Part II of "Chemical Knowledge in the New Testament" will be found in the March issue of THIS JOURNAL]

Elastic Silica: A Demonstration

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RECENTLY two interesting and informative accounts,[1, 2] have been given of the role of silicon, the second most abundant element, in polymeric chemistry. A particular aspect is the combination of silicon with oxygen and alkyl groups to obtain complex molecules which are plastic to slowly applied forces and elastic to rapidly applied forces. The name "bouncing putty" has been applied to cover those materials which flow like a viscous liquid under a static load, but rebound like rubber when thrown.

During a phase of some silicon research the writer prepared a material with rubber-like qualities from ordinary water glass. Mindful of the possibility of a lecture demonstration on a topic of contemporary interest, a procedure was devised for readily showing some elastic properties of silica.

It was observed that addition of an alcohol to commercial water glass caused a solid to precipitate which can be worked with the fingers into a sphere that bounces like rubber when dropped. The relative quantities of materials do not seem to be critical. A satisfactory aggregate may be formed by diluting 10 ml. of commercial sodium silicate solution ("egg preserving solution") in a small beaker to about 20 ml. with water, and then adding slowly with stirring about 10 ml. of 95 per cent ethanol. A metal rod with spatula tip is convenient for stirring.

After the mixture has solidified, the solid may be removed with the fingers, or with the spatula, and pressed into a ball of about one inch in diameter. It is advisable to have water flowing from a faucet close by to wash the excess caustic from the sphere and the fingers. Some demonstrators may find it desirable to wear rubber gloves, but the writer felt no ill effects after preparing 10 spheres. The knack of producing a ball that will bounce when dropped will be readily obtained after one or two attempts.

In a classroom demonstration it is suggested that several spheres be prepared so that in addition to the bouncing or elastic property, the plastic effect may also be observed. A freshly prepared sphere when placed on a flat surface will settle and in a few minutes a flat side will develop. The process may be repeated several times by reforming the sphere.

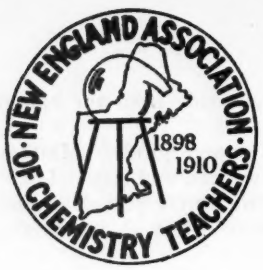
Prolonged exposure of this form of silica to the atmosphere gives rise to a drying effect which causes the mass to become granular and fragile. The elastic property, however, diminishes slowly, and even when the mass is hard, it will bounce some if dropped. Finally it becomes brittle and shatters upon hitting a surface.

The role of alcohol in producing the elastic silica is not clear. It may be a catalyst but there is some evidence that the alcohol becomes a part of the mass and may be in the form of an organosilicon polymer. The solid dissolves fairly readily in water to form a solution which is alkaline to litmus but which does not precipitate silicic acid upon treatment with small or large quantities of hydrochloric acid. Other alcohols will produce the same effect and even the alcohol amines will produce elastic silica when added to water glass. In fact a sphere produced with triethanolamine seemed to be more plastic than one prepared with ethanol.

Other demonstrations of the properties of silica may be visualized from the thoughts expressed here. More particularly the formation of thin films of a silica-like character can be produced on metals by painting the surface with a solution prepared by dissolving some of the solid in water and then allowing the water to evaporate.

[1] ROCHOW, E. G., "The organosilicon polymers," *Chem. Eng. News*, **23**, 612 (1945).

[2] COLLINGS, W. R., "New Dow Corning plant produces silicones at Midland," *ibid.*, **23**, 1616 (1945).



Report of the NEW ENGLAND ASSOCIATION of CHEMISTRY TEACHERS

Activated Carbon[1]

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TO THE man in the street, activated carbon is usually something he has heard about vaguely. If pressed, he may recall that it is the material used in gas masks, or, if he is of a convivial nature, he may remember that it found surreptitious use during the prohibition era for making corn liquor reasonably palatable. Activated carbon belongs to that rather sizable class of products which never reach the ultimate consumer, but are used in large quantities in the manufacture of the items and materials of everyday living: foods, medicinals, clothing, household goods, automobiles, and other accessories.

The next reaction of the man in the street is to ask what "activated" means. Like many other innocent-sounding questions, this is quite a poser; it cannot be answered in a few short words.

In the early nineteenth century, it was found that charred animal bones have the property of removing colored substances from the juice of sugar cane, without removing any of the sugar at the same time. It was found also that wood charcoal has a similar property, and that this property, which is called "adsorption," can be enhanced by careful control of the carbonizing process. "Activation" is the term applied to the maximum development of adsorptive capacity.

Commercially, there are two distinct types of activated carbon. One type is made for the adsorption of gases; in wartime, it finds a large scale use in gas masks, where its function is the adsorption of chemical warfare agents from the air breathed by the wearer. In time of peace, this type of activated carbon is used to recover valuable solvent vapors from air, as explained in greater detail later in this discussion.

The other type of activated carbon is designed for use on liquids, for the removal of color, taste, odor, and other impurities. These carbons are generally known as decolorizing carbons.

Raw Materials. The gas and vapor adsorbent carbons were formerly made from coconut shells because of the hard, dense structure of these shells. Since the Japanese war, other nut shells have been used, and methods have been developed for using softer charcoals, which are given the necessary hardness and density by the use of a binder.

The decolorizing carbons are made from animal bones, from wood charcoal, from lignite, and from paper mill waste liquor, which contains lignin and cellulose degradation products.

Method of Manufacture. The primary objectives in activated carbon manufacture are the production of a maximum adsorption surface, and the conditioning of that surface for maximum adsorption per unit area. Secondary objectives are hardness and density for the gas adsorbent carbons, and density, filterability, and purity for the decolorizing carbons.

The carbonization step, in which surface area is developed, is a process of destructive distillation, *i. e.*, the raw material is subjected to high temperature with exclusion of air. Organic matter is thereby broken down into volatile products, which are driven off, and a carbonaceous residue of highly porous structure; the pore volume of this carbon is the space previously occupied by the volatilized matter and is approximately 50 per cent of the volume of the carbon.

Conditioning of the surface is essentially a process of mild oxidation at high temperature; at such temperature steam and carbon dioxide are suitable oxidizing agents. Air may be admitted to the activating furnace in small quantities.

With some activated carbons, the carbonization step is preceded by chemical treatment at high temperature for preliminary breakdown of organic matter. The agents used are all strong dehydrators, such as phosphoric or sulfuric acid, and zinc chloride. Their dehydrating action is sufficiently powerful to break down organic substances into water and other degradation products. After chemical treatment, these carbons are subjected to destructive distillation and surface conditioning as described above.

The surface area of a properly activated carbon is enormous. It is on the order of 50 acres per pound. This area is essentially that of the internal pore structure of the carbon. The pores and capillaries of this structure are of substantially molecular dimensions. With the pore volume 40 to 60 per cent of the carbon

[1] Presented before the Seventh Summer Conference of the New England Association of Chemistry Teachers, Massachusetts State College, Amherst, Massachusetts, August 12, 1945.

volume, and the pore dimensions of molecular order, it can readily be seen why the pore and capillary wall area sums up to such large values.

After activation has been completed, the carbon must be crushed, ground, and sieved to produce granules or particles of suitable size. The gas-adsorbent carbons are ordinarily supplied in mesh ranges such as 4 × 6 or 12 × 20. (4 × 6 mesh means granules which will pass through a screen having four openings per linear inch, and will be retained by six openings per inch.)

The decolorizing carbons are usually ground to a very fine powder, such that 70–98 per cent will pass through a 325-mesh screen. Particles of such size are smaller than 45 microns, which is 0.002 inch. The number of particles in carbon so ground is approximately 5×10^{13}, or fifty thousand billion per pound. The purpose of such fine grinding is to make the internal surface of the carbon quickly accessible to liquids being purified with it. Care must be exercised in the grinding operation, to produce particles of such shape and of such particle size distribution, that good filterability is imparted to the carbon.

The gas-adsorbent carbons are ready for use after crushing and screening to proper granule size. In most cases, the decolorizing carbons must be washed with acid and water to remove extractable inorganic matter associated with them because of the raw material from which they are made. Acid washing removes extractable iron, aluminum, and calcium compounds; water washing removes the acid, as well as sodium salts, sulfides, chlorides, etc. A carefully washed carbon should contain only a few tenths of a per cent of matter extractable with water, and less than one per cent extractable with hot mineral acid, using prolonged leaching.

Elimination of extractable inorganic matter is necessary to avoid contamination of the liquids which the carbon is called upon to purify.

Methods of Application. Industrially, the gas-adsorbent carbons are used to recover solvent vapors from air. Automobile bodies, for example, are painted with spray guns in specially constructed booths from which air is drawn off through large ducts. The vehicle for the paint is a volatile solvent, which is lost into the air through evaporation from the painted surface. The air containing this solvent vapor is passed through beds of granular activated carbon which selectively adsorbs the vapor.

When the limit of adsorptive capacity is reached, the solvent is recovered by blowing steam through the carbon; the vented steam carries the revolatilized solvent vapor to a condenser where both return to liquid form. If the solvent is immiscible with water, it is readily separated by drawing off the solvent layer; if it is miscible, it must be separated by distillation. Extremely small concentrations of solvent vapor can be recovered from air by this procedure.

Powdered decolorizing carbons are applied by stirring a small percentage of carbon with the liquid being treated. The dosage may range from 0.01 to 5 per cent on weight of liquid. Stirring should be active, and should produce motion of carbon relative to the liquid, so that the suspended particles may thoroughly sweep all portions of the liquid. The time required for adequate contact may range from 10–30 minutes, although several hours may be required in exceptional cases. Treatment may be conducted at as high a temperature as the nature of the liquid permits; through reduction of viscosity, treatment at elevated temperature hastens adsorption equilibrium and may make adsorption more complete by permitting more complete penetration of the liquid into the internal pore structure of the carbon particles.

When adsorption equilibrium has been reached, the carbon is removed from the liquid by filtration. In this step the bulk density of the carbon plays an important part. A carbon of high density will occupy minimum volume in a filter of given solids capacity and thereby permit maximum filter runs before cleaning is necessary. Also, carbon of high bulk density will retain a minimum volume of the filtered liquid at the end of filtration, a factor of great importance when the filtrate is valuable.

In certain applications, such as in purity maintenance of dry-cleaning solvent or of electroplating solutions, treatment is effected by first depositing the carbon as a pre-coat in a filter and then circulating the liquid continuously through the carbon. This procedure, which permits brief contact only between carbon and liquid, is effective where the amount of impurity does not exceed a very low level; the function of the carbon is the continuous removal of such impurity as fast as it is introduced into the liquid.

In municipal water purification plants, powdered activated carbon is used for the elimination of odor and taste. Carbon dosages on the order of 10 to 20 pounds per million gallons ordinarily suffice. The carbon is applied by dispersion in large settling basins where a contact period of one to four hours is afforded before the carbon settles out. Carbon that is carried through the settling basins is caught on sand filters.

Granular activated carbons are applied by percolating the liquid to be treated through a bed of the carbon. Bone charcoal is still used in this manner in the sugar-refining industry. As the carbon continues in use, it gradually becomes "spent," *i. e.*, its adsorptive surface becomes coated with color bodies from the sugar liquor, and eventually the char tower must be cut out of service for regeneration. This is done in a furnace at high temperature; the process is essentially similar to the original activation of the carbon. The adsorbed organic matter is driven off with little or no air admitted to the furnace, since care must be taken not to burn the "primary" carbon. "Secondary" carbon from the adsorbed organic matter is believed to account for part of the adsorptive capacity of repeatedly regenerated bone char.

Granular activated carbon made from lignite is extensively used for odor and taste removal from industrial water supplies. Here again the water to be

treated, which must be completely pre-clarified, is percolated through a bed of the carbon. The life of such a bed is much longer than the bone char towers used in sugar refining; whereas the latter may have a service life measured in days, water treatment filters seldom become spent within one year, and a number have been known to last as long as five years. This longer life arises from the fact that the impurities removed from water are of extremely low concentration, so that a cubic foot of carbon in continuous service for one year can treat 250,000 gallons of water. Because of its long service life, such carbon need not be regenerated to justify its cost.

Within the last few years a most interesting new method of use has arisen for activated carbon. This is in the production of penicillin and similar antibiotic agents. Penicillin is the exudate discharged by molds such as *Penicillium notatum;* after culture of the mold has been completed, the penicillin is found in very dilute concentration in the culture medium. Carbon of very high activity and purity is used to adsorb the penicillin; after filtration from the culture broth, the penicillin is recovered in concentrated form by elution of the carbon with a suitable solvent. This method is now being used commercially also on the new antibiotic agent, streptomycin, and experimental work is being done on the concentration of certain hormones by the same procedure.

Products Treated with Activated Carbon. The largest field of use for activated carbon is in the refining of cane, beet, and corn sugar. The cane and corn sugar industries still use bone char extensively, but within the last decade many refineries have been converted for use of the "vegetable" carbons, *i. e.*, those made from materials of plant origin, such as lignite, wood charcoal, or paper mill waste liquor. The beet sugar industry in the United States uses the powdered type almost exclusively.

The function of carbon in sugar refining is typical of many other applications. Sugar is produced by Nature in cane stalks and beet roots, but is, of course, associated in the plant cells with many other substances, both organic and inorganic. The problem in sugar refining is to separate the sugar from these associated materials. Removal of fiber and other coarse insoluble matter from the raw sugar juice is simple; this is accomplished by screening and filtering. Removal of a part of the dissolved and colloidal matter can be effected by flocculation with lime, phosphoric acid, and similar agents. As the juice progresses through the refinery, however, and particularly as it is concentrated by evaporation, residual impurities carry through with it and tend to darken under the influence of heat. Since the final objective is white crystalline sugar of practically 100 per cent purity, these associated color bodies and other impurities must be removed before the sugar liquor receives its final boiling to produce "grain" or sugar crystals. It is these substances, both colored and noncolored, which the carbon removes by adsorption.

Other products of agricultural origin with which the carbon has a similar function are pectin and cider vinegar from apples; citric acid from cull citrous fruits; quinine from cinchona bark; corn, cottonseed, linseed, soya bean, and other oils from the respective oil seeds; hydrogenated fats; glycerol, as a by-product in soap manufacture, which uses vegetable and animal fats; lactose from milk; sodium acetate from wood distillation; agar agar and sodium alginate from seaweed; wine, whiskey, rum, and gin; and a host of others.

Another large group of products treated with activated carbon are organic chemicals which are made synthetically. In many syntheses, side reaction products are formed, and these may have undesirable colors, odors, or tastes. Among synthetic products treated with carbon are intermediates used in making nylon and many dyes; sulfa drugs, atabrine, and photographic chemicals are purified both in the intermediate and finished stages. Synthetic vanillin, epinephrin, vitamins, and many pharmaceuticals are brought to the necessary high state of purity by activated carbon treatment.

Attention has already been called to the fact that the adsorptive action of the decolorizing carbons is not limited to colored substances. In numerous instances, the impurities adsorbed by carbon are entirely colorless, tasteless, and odorless. When the product being purified is sold in crystalline form, for example, it is frequently necessary to remove impurities that cause poor crystal formation or give a dull, lusterless appearance to the crystals. Such impurities may also inhibit crystallization itself and give a poor yield of crystals. Instances are known in which activated carbon treatment has resulted in the doubling of the crystal yield, through adsorption of impurities of this type.

Adsorption Theory and Equations. The adsorption and retention of substances at the carbon surface involve, of course, an expenditure of energy. The expendable energy at a surface is conceived to exist there because of the following conditions.

A surface is essentially a boundary between two dissimilar forms of matter. It is the outermost molecular extension of a solid or liquid. Below the surface the molecules are uniformly surrounded by other molecules of the same kind, and there is a balancing of the molecular forces between them. At the surface, however, the outermost molecules have no similar molecules beyond them, so that part of their molecular forces are free and can be exerted toward matter coming into contact with them. The reason why carbon can be made so powerfully adsorptive is probably twofold: first, it is relatively easy to develop a very large carbon surface by subjecting carbon compounds to the molecularly disruptive force of destructive distillation; and second, carbon is a tetravalent element, capable of forming both positive and negative atomic linkages. It is significant that the only other commercially useful adsorbents are compounds of silicon, which is also tetravalent, and just below carbon in the periodic

table, and compounds of aluminum, a trivalent element just to the left of silicon.

The capillary structure of activated carbon, because of its molecular dimensions, further intensifies the energy exerted by the surface; a molecule of adsorbed substance is acted upon not merely by a single surface, but by the opposite wall of the capillary (or fissure) as well.

The relationship between amount of material adsorbed and surface energy is given by the Gibbs adsorption equation:

$$1/S = -(C/RT)\cdot(d\sigma/dC)$$

in which 1 represents one mol of adsorbate, S is the area in square centimeters on which the mol is adsorbed, C is the equilibrium concentration of unadsorbed substance in the phase in contact with the surface, R is the gas constant, T is the absolute temperature, and $d\sigma/dC$ is the rate of change of surface energy with C, sigma being the surface energy in ergs per square centimeter.

Unfortunately, in the case of activated carbon, this equation cannot be put to practical use. It is not yet possible to measure accurately the surface energy of a solid with a large internal surface, nor is it possible to determine the surface area which is actually accessible to the substance being adsorbed. The matter is also complicated by the fact that adsorption is not necessarily confined to a monomolecular layer on the adsorption surface; there is abundant evidence that multimolecular layers are formed in many cases. There is, furthermore, no assurance that the entire surface is at a uniform energy level; it appears highly probable that the surface is made up of spots of varying degrees of "activity" from a maximum to zero. There is no information on the gradation and distribution of these spots.

Since the strictly theoretical equation cannot be applied, it is necessary to fall back on empirical equations. The two most useful are the Langmuir equation and the Freundlich equation. Both are known as isotherm equations, *i. e.*, they describe adsorption at constant temperature. The Langmuir equation is useful in gas and vapor adsorptions, the Freundlich equation for adsorption from solution.

The Langmuir equation is usually written

$$V = V_m bp/(1 + bp)$$

In this, V is volume adsorbed, V_m is the volume adsorbed when the surface is covered completely with a monomolecular layer of adsorbate, b is a constant, and p is the pressure at which the adsorption reaches equilibrium.

By rearrangement of terms, the Langmuir equation becomes

$$p/V = (1/V_m b) + (p/V_m)$$

in which form it can be used to test data being evaluated. The test consists in ascertaining whether p/V plotted against p is a straight line. If a straight line is obtained, the Langmuir equation is applicable to the data, and the constants V_m and b can be calculated from the slope and intercept of the line. The Langmuir constants are well defined physical quantities,[2] and the equation is empirical only in the sense that certain simplifying assumptions are made in its derivation. Langmuir assumed, first, that the forces of interaction between gas molecules adsorbed at a surface are negligible, and second, that a gas molecule striking a point on an adsorbent which is already occupied by another molecule, is not adsorbed but elastically reflected, *i. e.*, that adsorption is entirely monomolecular. He also assumes that the entire adsorptive surface is of uniform character.

That these assumptions are reasonably well justified is attested by the fact that the Langmuir equation is applicable in a wide range of gas and vapor adsorptions, not only on carbon, but on other adsorbents as well.

The Freundlich equation is written

$$X/M = Kp^{1/n}$$

for the adsorption of gases and vapors, and

$$X/M = KC^{1/n}$$

for adsorption from solution.

In these equations, X is quantity of substance adsorbed, and M is the weight of carbon on which the adsorption occurs. X/M is therefore adsorption per unit weight of carbon. p and C are pressure and concentration, respectively, at adsorption equilibrium, of unadsorbed substance in the phase in contact with the carbon; K and $1/n$ are constants. It is useful to consider X/M as expressing the concentration of adsorbate on the carbon; under that concept, the Freundlich equation is a distribution equation relating the concentration of adsorbate in the adsorbed and unadsorbed states. In logarithmic form the equation becomes $\log X/M = \log K + 1/n \log C$ or $\log p$, a straight line of the form $y = a + bx$. For this reason the Freundlich equation plots as a straight line on logarithmic paper; K is the intercept at $C = 1$, and $1/n$ is the slope of the line.

K and $1/n$ are particular constants, determined by both the particular carbon and the particular adsorbate used in determining the data to which they apply. It is not possible to predict from their values what course adsorption by the same carbon will take on another adsorbate, nor how the particular adsorbate will be adsorbed on another carbon. Numerically, K may have any positive value; $1/n$ likewise is always positive; its values may range from just above zero to eight or ten. The normal range is about 0.2 to 1.0.

Qualitatively, K is thought to be an index of the capacity factor of adsorption, *i. e.*, the adsorptive area involved, and $1/n$ can be considered as an index of the intensity factor, or energy per unit area. An adsorption characterized by a low $1/n$ value indicates a

[2] The derivation of these constants and of the equation itself is beyond the scope of this discussion, but the interested reader is referred to "The Adsorption of Gases and Vapors," Volume 1, by Stephen Brunauer, for an excellent exposition of this important equation.

readily adsorbed substance and, conversely, a high $1/n$ value indicates poor adsorbability.

As may be expected with an empirical equation, the Freundlich isotherm is linear within definite concentration limits only, beyond which the plot exhibits definite curvature. In commercial applications, however, the plot is so universally linear that departure from a straight line can be safely taken as an indication either of error or of abnormality. The equation is exceedingly useful in evaluating activated carbons for a particular application, for establishing the optimum conditions of treatment, for confirming the uniformity of successive shipments of carbon, and for many purposes.

Relation of Activated Carbon to Other Adsorbents. Mention has already been made of adsorbents which are compounds of silicon and of aluminum. Among the most noteworthy of these are silica gel, which is silicon dioxide (silica), and calcined alumina (aluminum trioxide). These are characterized primarily by their powerful adsorptive capacity for water vapor; this property of silica gel has led to its widespread use as a moisture adsorbent packing for metal parts used in war. By packing these with silica gel, ruinous rusting is prevented which could otherwise be done only by packing the parts in heavy grease. Parts packed in silica gel can be assembled immediately on unpacking, a vital factor with supplies promptly needed at landing beaches and in similar situations.

A number of clays, which are essentially complex silicates of aluminum, calcium, and magnesium, also have adsorptive properties. These activated clays are particularly suitable for decolorization and purification of organic liquids, such as petroleum, in the refining of which huge tonnages are used. The activated clays exert little or no adsorptive capacity in aqueous solutions.

In all these adsorbents, the surface forces are in general of similar nature to those operative on activated carbon. In a more specialized class are the so-called exchange adsorbents. The best known of these are the base-exchange zeolites, which are complex silicates, with a labile sodium atom that can be exchanged for calcium in the water-softening process. Recently, organic exchange adsorbents have been developed, in both cation and anion exchange types. These are synthetic resins; the cation exchange resins have a labile hydrogen in their molecular structure, which can exchange with other cations (except the NH_4^+ radical). The anion exchange resins have a labile hydroxyl group, which can be exchanged for other anions. Water containing dissolved mineral matter, which is treated successively with cation and anion exchange resins, has its mineral content exchanged for H^+ and OH^-, *i. e.*, for water.

It will be seen, thus, that the various adsorbents, of which activated carbon is an important example, play a large role in our industrial civilization and, almost unknown to the ultimate consumer, serve him on every side through their part in helping to produce the many items of everyday living.

NOTES

The Association is no longer able to contact the following deferred members by means of the addresses that we now have. Anyone who knows the present address of one or more of these persons is requested to communicate with the Secretary, Miss Dorothy W. Gifford, Lincoln School, Providence 6, Rhode Island.

Lt. Laurence E. Bohrer
Capt. Wilbur E. Bradt
Mr. James F. Davison
Lt. Col. Harry B. Feldman
Lt. Stanley C. Fisher
Ensign Neale E. Howard
Mr. Edmund R. Johnson
Mr. E. Gordon Rice
Lt. L. Ashley Rich
Corp. Richard I. Savage
Dr. Alberto F. Thompson, Jr.
Lt. Albert C. Wright
Lt. Wilton Brown

NEW MEMBERS

Lenna M. Peabody, Winchester Senior High School, Winchester, Massachusetts

John Gammons Read, Rhode Island College of Education, Providence, Rhode Island

Ervin Stuart, Braintree High School, Braintree, Massachusetts

Mr. Ralph E. Brierley, Cranston Senior High School, Cranston, Rhode Island

Mr. Raymond C. Colwell, Rhode Island School of Design, Providence, Rhode Island

Mr. James Tiffany Leary, Naugatuck High School, Naugatuck, Connecticut

Miss Jane R. Martin, Rogers Hall, Lowell, Massachusetts

Miss Lillian G. Murdock, Brookline High School, Brookline, Massachusetts

Mr. Albert B. Nelson, Rhode Island State College, Kingston, Rhode Island

Miss Marguerite Padula, Canton High School, Canton, Connecticut

Brother Romuald, Mount St. Louis College, Montreal, Canada

Mr. Edward P. Sawin, Cranston High School, Cranston, Rhode Island

Sister M. Emily, S.S.J., Regis College, Weston, Massachusetts

Sister M. Juliana, O.S.B., St. Anthony High School, Washington, D. C.

Sister M. St. Eustelle, St. Marie High School, Manchester, New Hampshire

Mr. J. Harold Smith, Massachusetts State College, Amherst, Massachusetts

SCHEDULE OF MEETINGS

235th meeting, March 16, 1946, College of Our Lady of the Elms, Chicopee, Massachusetts

236th meeting, May, vicinity of Boston, Massachusetts

Eighth Summer Conference, August 19–24, 1946, Middlebury College, Middlebury, Vermont

RECENT BOOKS

ORGANIC SYNTHESES. *Werner E. Bachmann*, Editor-in-Chief. Volume 25. John Wiley and Sons, Inc., New York, 1945. vi + 120 pp. 14.5 × 23.5 cm. $2.00.

This latest addition, Volume 25, of a series of annual volumes gives the equations for the reactions, procedures for production with accompanying notes, and other methods of preparation for 37 different organic compounds. The suggested directions have been further checked or verified by competent referees. The cumulative subject index comprises all material from Volumes 20 through 25 of this series, the Collective Volumes 1 and 2 having included all previous preparations.

Methods for the preparation of the following compounds are included: acrolein acetal and β-ethoxypropionaldehyde acetal, 2-amino-4-nitrophenol, benzoylacetanilide, *o*-*n*-butoxynitrobenzene, *n*-butylbenzene, 1-*n*-butylpyrrolidine, β-carbomethoxypropionyl chloride, 2-chlorocyclohexanone, α-cyclohexylphenylacetonitrile, diazomethane, 2,5-dimethylmandelic acid, 2,4-dimethylthiazole, dithizone, ethyl benzalmalonate, ethyl (1-ethylpropenyl)-methylcyanoacetate, ethyl (1-ethylpropylidene)-cyanoacetate, *o*-eugenol, furylacrylic acid, β-*d*-glucose-2,3,4,6-tetraacetate, *m*-hydroxybenzaldehyde, isobutyramide, isobutyronitrile, malononitrile, mesitylacetic acid, methyl ω-cyanopelargonate, methyl sebacamate, naphthoresorcinol, 2-nitro-4-methoxyaniline, nitrosobenzene, 4-penten-1-ol, *p*-phenylazobenzoic acid, *p*-phenylazobenzoyl chloride, β-phenylethyldimethylamine, phenylpropargyl aldehyde, and sebaconitrile and ω-cyanopelargonic acid.

Chemists, who have long since learned to await enthusiastically the appearance of each new volume of this popular and useful series, will not be disappointed with the latest addition. While this book has been manufactured in accordance with the recommendations and restrictions of the War Production Board in the interest of the conversion of paper and other important war materials, the appearance and quality of this volume in every respect measures up to prewar standards nevertheless. The general plan, arrangement, and quality are identical with previous members of the series. All organic chemists and technical libraries will purchase this volume as an essential addition to their previous files which have now grown to be the most valuable and extensive accumulation of accepted methods of organic syntheses in the English language.

RALPH E. DUNBAR

NORTH DAKOTA AGRICULTURAL COLLEGE
FARGO, NORTH DAKOTA

ORGANIC OXIDATION-REDUCTION REACTIONS. *William C. McGavock*, Professor of Chemistry, Trinity University. Second Edition. Published by the author, 1945. viii + 141 pp. 27 figs. 21.5 × 28 cm. $3.75.

This book is intended as an aid to the student in the interpretation of organic oxidation-reduction reactions by the instrumentation of oxidation-number assignments and a system of "electron accounting." The use of electrochemical theory in this specific manner appears to be important when the author indicates that in one well-known organic textbook, which he examined, slightly more than half of the reactions discussed were oxidation-reduction reactions. The application of electronic theory is quite inclusive as 500 type reactions are presented, along with 400 balanced equations. Some of these equations are not of oxidation-reduction reactions.

The general rules for the assignment of oxidation numbers are those that have been applied for many years in the interpretation of inorganic reactions. The author considers that fractional numbers are not objectionable. The attachment of electronegative atoms (or groups) to a carbon atom results in a "loss" of electrons by the carbon atom, and the attachment of electropositive atoms (or groups) causes a "gain" of electrons by the carbon atom. An electronegativity chart is included in which hydrogen and the methyl group are slightly more electropositive than carbon (the methyl group is electronegative in respect to hydrogen). The conventional aryl group (Ar) is slightly more electronegative than carbon. The oxidation number of the methyl group in methane is −1, the methyl groups in propane and isobutane are each +1, and the methyl groups in ethane are 0. The system of assignment as applied to molecules containing one carbon atom is, of course, straightforward. When applied to molecules of two carbons the conventional rules give an average oxidation number to the carbon atoms. The author, by using the concept of apparent electronegativity and electropositivity, assigns an oxidation number to each carbon atom. In the case of the unsymmetrical molecule, ethyl alcohol, the author assigns an oxidation number of −2 to each carbon atom and he shows that qualitatively both atoms are the same in respect to attachment of electronegative and electropositive atoms or groups of atoms. The system formulated for molecules of three carbon atoms may appear somewhat arbitrary. No attempt is made to adapt the scheme to compounds containing four carbon atoms. The 25 charts in the book illustrate most of the simple reactions that involve type molecules of the more common classes of compounds. These charts are very helpful and neatly formulated. There is a section presenting the various techniques employed in balancing oxidation-reduction reactions.

An application of all the material in the book to a course in elementary organic chemistry might be rather difficult. The amount of time that could be given to a complete treatment of oxidation-reduction is limited due to the wealth of material that must be presented in the classical manner; however, the reviewer is of the opinion that a portion of the material could be used profitably. More advanced students would undoubtedly be able to appreciate the book more fully and also digest its contents with less assistance. Many students may feel that the price is excessive, as the book is planographed and has a paper binding. The book is provocative and should be of interest to many teachers even though they may not intend to use the book in their classes.

DONALD C. GREGG

AMHERST COLLEGE
AMHERST, MASSACHUSETTS

THERMODYNAMIC PROPERTIES OF AIR. *Joseph H. Keenan*, Professor of Mechanical Engineering, Massachusetts Institute of Technology, and *Joseph Kaye*, Assistant Professor of Mechanical Engineering. John Wiley and Sons, Inc., New York, 1945. iii + 273 pp. 18.5 × 26 cm. $2.25.

The authors point out, "The need for a working table of the thermodynamic properties of air has been emphasized recently by the rapidly growing interest in the gas turbine. . . . Computation of certain . . . processes, . . . such as the heating of air in a regenerator or the expansion of air and similar gases from states of high temperature, involve laborious integrations if tabulated properties are not available."

Herein lies the great need for this work. Its value may be judged by mentioning the contents. There are thirteen tables: Table 1 is the principal table and contains thermodynamic properties of air, at low pressures, from 300° to 6500°F., absolute in intervals of 1°. Table 2 gives values of $R \log_e N$ for values of N from one to ten. Table 3 contains specific heats, ratios of specific heats, velocity of sound, maximum flow per unit area, viscosity, thermal conductivity, and Prandtl numbers for air from 200° to 6400° absolute. Table 4 contains the value of terms in formulas in which the quantities of Tables 5 to 9 appear. Table 5 has the polytropic functions of pressure ratio, $n = 1.4$; Table 6 the values of $r^{1/n}$, variable n; Table 7 the values of $r^{\frac{n-1}{n}}$, variable n; Table 8 the values of $1\sqrt{1-r^{\frac{n-1}{n}}}$, variable n; Table 9 the values of $r^{1/n}\sqrt{1-r^{\frac{n-1}{n}}}$, variable n; Table 10 $\log_{10} N$; Table 11 $\log_e N$; Table 12 conversion factors; and Table 13 temperature conversions.

Sources and methods in the development of Table 1 are given.

There are ten interesting examples illustrating the use of the tables. These are: compression of air in a steady flow; expansion of air through a nozzle in a steady flow; change in entropy; the pressure in a turbine stage; reversible adiabatic steady flow; polytropic process; discharge of air from a closed container; gas turbine; Otto engine; and Diesel engine.

Special commendation is deserved for excellency of arrangement and clarity of type. These aid considerably in the use of the tables.

The authors have in progress an extension of the present data to cover the properties of air-fuel mixtures for hydrocarbon fuels and their products of combustion, a book which will be eagerly awaited.

BERNARD LEWIS

ORDNANCE DEPARTMENT
WASHINGTON, D. C.

PROBLEMS FOR GENERAL CHEMISTRY AND QUALITATIVE ANALYSIS. *C. H. Sorum*, Professor of Chemistry, University of Wisconsin. George Banta Publishing Company, Menasha, Wisconsin, 1945. viii + 95 pages. 15.5 cm. × 23.5 cm.

The problems are designed for a sequence in which general chemistry and qualitative analysis are covered in one year and those involving hydrolysis, dissociation of complex ions, and oxidation-reduction equilibria have not been emphasized. An interesting innovation is a group of problems on "Radioactive Change and Artificial Transmutation." The arrangement of problems in each section is in the order of increasing difficulty, facilitating selection of review examples. In an effort to recall to the student his rudimentary knowledge of arithmetic, Chapter II is devoted to "Division, Multiplication, and Fractions" in which grocery store examples are used to give him an intuitive approach to the solution of chemical problems. Admissions officers may not like to admit it, but most teachers of college freshmen will testify that this chapter is not out of place in a college textbook! The student is urged to use a slide rule for his computations and to express his numerical answer in the correct units. While the "factor-label" method of solving problems has not been adopted to as great an extent as is considered desirable by many, use of factors and units has been adhered to in all illustrative problems. This is a good book which can be recommended to college freshmen as a supplement to any text book.

LAURENCE S. FOSTER

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

CONSUMER CHEMISTRY. *John Chiocca* and *Robert van Reen*. Edited by *Sara Bent Ransom*, Instructor in Science, College High School, Upper Montclair, New Jersey. New Jersey State Teachers College, Upper Montclair, 1945. iv + 36 pp. 21.5 × 28 cm. mimeographed, paper covers, stapled binding. $0.75.

The book is a listing of charts, exhibits, films, slides, filmslides, pictures, publications, and recordings related to elementary chemistry. It is an extensive and useful list, notable in its omission of the JOURNAL OF CHEMICAL EDUCATION and the material sponsored by the Division of Chemical Education.

ELBERT C. WEAVER

PHILLIPS ACADEMY
ANDOVER, MASSACHUSETTS

DICTIONARY OF GEOLOGICAL TERMS (Exclusive of stratigraphic formations and paleontologic genera and species). *C. Mabel Rice*. Edwards Brothers, Inc., Ann Arbor, Michigan, 1945. iv + 464 pp. 15 × 23 cm. $6.00.

This dictionary contains a summary of terms from original sources, often including interpretations. It is a valuable work for chemists and others interested in the composition of natural materials. Detailed reading reveals thorough and accurate coverage.

ELBERT C. WEAVER

PHILLIPS ACADEMY
ANDOVER, MASSACHUSETTS

MANOMETRIC METHODS as applied to the measurement of cell respiration and other processes. *Malcolm Dixon*, University Lecturer in Biochemistry, University of Cambridge. 2nd Edition. The Macmillan Company, New York, 1943. xiv + 155 pp. 20 figs. 13 × 19.5 cm. $1.75.

This second edition is a revision of the first in the light of recent improvements in technique. It gives the complete theory and full practical details of manometric methods used in nearly all biological, biochemical, physiological, and bacteriological laboratories. The different types of manometers used are first discussed and then the various methods of measuring respiration.

ELEMENTARY STATISTICS. *Hyman Levy*, Professor of Mathematics, Imperial College of Science, London; *E. E. Preidel*, Assistant Lecturer in Mathematics, Imperial College of Science, London. The Ronald Press Company, New York, 1945. vii + 184 pp. 29 figs. 13 × 19.5 cm. $2.25.

This book is concerned with some of the methods of analyzing facts and figures so that as much as possible of the information they contain can be presented in a just way.

LETTERS (*Continued from page 89*)

creases upon burning and if the amount is always the same for similar experiments with the same materials. This leads to the law of definite proportions. The law of multiple proportion can be postponed for the time. The law can then be tested by laboratory work. The attempt to explain these observations will lead to the atomic theory. The real meaning of an hypothesis, theory, and law can be explained and justly evaluated. This development is worth much time at the beginning of the year precisely because it illustrates the scientific method so well and puts such a firm foundation under the rest of the course. It is a unit in itself, completely satisfying to the student, and adequately illustrates the method. There is no need at this time to complicate it with the truly difficult question of atomic weight determinations. Other equally detailed examples of the scientific method can be given later in establishing the kinetic molecular hypothesis and other basic concepts.

Never should the teacher be illogical. Bad logic has no place in any classroom. But explanations which are incomplete are not necessarily lacking in logic. Two or more theories worked out in detail according to the scientific method give the teacher the right to teach much else without details of method, because they are impossible under the circumstances, over the heads of the students, or too time-consuming to merit such treatment. Such a science teacher is neither traitor to his method nor illogical.

(REV.) GERALD F. HUTCHINSON, S.J.

CHEVERUS HIGH SCHOOL
PORTLAND, MAINE